

Solar Silicon via Improved and Expanded Metallurgical Silicon Technology

QUARTERLY REPORT NO. 4

July 1977

L. P. HUNT, V. D. DOSAJ
and J. R. McCORMICK

DOW CORNING CORPORATION
Solid-State Research and Development Laboratory
Hemlock, Michigan 48626

JPL Contract NO. 954559

This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, under NASA Contract NAS7-100 for the U.S. Energy Research and Development Administration, Division of Solar Energy

The JPL Low-Cost Silicon Solar Array Project is funded by ERDA and forms part of the ERDA Photovoltaic Conversion Program to initiate a major effort toward the development of low-cost solar arrays

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DOW CORNING CORPORATION, MIDLAND, MICHIGAN 48640

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ABSTRACT

The goal of this program is to produce solar-cell-grade silicon at 3000 Mt/y for less than \$10/kg by 1986. The approach is to improve the quality of the 200,000-Mt/y process for producing \$1/kg, 98-% pure metallurgical silicon.

A completed preliminary survey of silica sources indicates that sufficient quantities of high-purity quartz are available in the U.S. and Canada to meet LSSA goals. Supply can easily meet demand for this little-sought commodity.

Charcoal, as a reductant for silica, can be purified to a sufficient level by high-temperature fluorocarbon treatment and vacuum processing. High-temperature treatment causes partial graphitization which can lead to difficulty in smelting.

Smelting of Arkansas quartz and purified charcoal produced kilogram quantities of silicon having impurity levels generally much lower than in MG-Si. Half of the goal was met of increasing the boron resistivity from 0.03 ohm-cm in metallurgical silicon to 0.3 ohm-cm in solar silicon.

A cost analysis of the solidification process indicate \$3.50-7.25/kg Si for the Czochralski-type process and \$1.50-4.25/kg Si for the Bridgman-type technique.

CONTENTS

	<u>Page</u>
Abstract.	i
Contents.	ii
I. Summary	1
II. Introduction.	3
III. Technical Discussion.	7
A. Task A - Raw Materials Identification and Selection .	7
1. Carbon Reductant.	7
a. Charcoal Purity	7
b. Charcoal Reactivity	9
2. Quartz and Quartzite.	11
B. Task B - Arc Furnace Studies.	13
1. Commercial-Scale Material Balance	13
a. Purpose	13
b. Experimental Procedure.	13
c. Results and Discussion.	15
2. Experimental-Scale Studies.	18
a. Purpose	18
b. Experimental Procedure.	20
c. Smelting Results and Discussion	23
d. Purity Results and Discussion	27
C. Task C - Vacuum Evaporation Studies	31
D. Task D - Unidirectional Solidification Studies. . . .	32
1. Czochralski-Type Technique.	32
a. Experimental	32
b. Cost Analysis.	32
2. Bridgman-Type Technique	44
a. Experimental	44
b. Cost Analysis.	44
E. Task E - Silicon Analysis	53
IV. Conclusions and Recommendations	55
V. References.	56
VI. Program Schedule.	58
VII. Plans	61
VIII. New Technology.	62
IX. Acknowledgement	62
X. Appendices.	63
A. Tables of Foreign and Domestic Contacts for High- Purity Silica	64
B. References for Silica Sources	75
C. Material Balance Data	78

I. SUMMARY

The overall goal of this contract is to produce solar-grade silicon (SoG-Si) costing less than \$10/kg at a rate of 3000 metric tons per year by the year 1986. The program approach involves improving upon and expanding the technology involved around the present-day commercial process for producing metallurgical-grade silicon (MG-Si). Such an approach is deemed to have high probability for success within the 1976-1986 framework since it involves working with an already existing process that has a USA capacity of about 200,000 metric tons per year, far in excess of the ERDA/JPL goal for SoG-Si. In addition, the silicon from this commercial process sells for \$1/kg, an order-of-magnitude less than the SoG-Si goal.

The overall program approach is to smelt higher-than-normal-purity quartz and charcoal in an upgraded arc furnace. The product silicon is then purified by segregating impurities via a crystal growth technique.

A preliminary survey was completed of high-purity silica sources and indicates that quartz of suitable purity is available in sufficient tonnage to supply the anticipated LSSA needs. The best sources identified to date are in Arkansas and British Columbia, Canada. Other potentially good sources are also available in the U.S. and Canada. There is a low demand for high-purity quartz at present such that little incentive has existed for developing suitable sources. There is general agreement that supply will meet demand.

Charcoal has been investigated as a carbon reductant for silica. Fluorocarbon purification of charcoal has indicated that temperatures in excess of 2000 °C are required to reduce the levels of B and P below the 5-10 ppmw range. Vacuum treatment of the charcoal, however, allows this temperature to be reduced to the 1500-2000 °C range. Other impurities are not a problem.

Smelting experiments with Arkansas quartz and purified charcoal (2000 °C) provided silicon having a resistivity (due to boron) of 0.09 ohm-cm. This is half of the goal of purifying MG-Si (0.03 ohm-cm) to SoG-Si (0.3 ohm-cm). Most other impurities were reduced by more than one order of magnitude compared to their levels in MG-Si. Smelting

difficulties were experienced with charcoal purified at high temperatures due to its partial graphitization. This may result in production of the wrong structural form of the intermediate silicon carbide.

The 0.09 ohm-cm produced silicon was subjected to purification using the Czochralski growth technique. Impurities, except for B and P were measured to be below the limits of detection of emission spectroscopy (5-10 ppmw). Based upon previous work, it is projected that these impurities are near the ppbw level, sufficient to meet any specifications for solar-grade silicon.

An impurity balance was performed on a commercial-scale arc furnace. Carbon was found to contribute the major share of impurities, the most coming from coal. The yield of impurities in MG-Si from raw materials was found to vary from 14% for phosphorus to 95% for vanadium. Yield was observed to be inversely proportional to the vapor pressure of the elemental impurity.

Cost analyses were made of the two unidirectional solidification processes being investigated. Based on the various parameters considered, the cost of a Czochralski-type process was calculated to range from \$3.50-7.25/kg Si. The Bridgman-type process costs were \$1.50-4.25/kg Si.

Evaluation of data via emission spectroscopy at the low levels required in this program pointed out the difficulties of using such data to make clear-cut decisions.

II. INTRODUCTION

This 14-month contract began on July 31, 1976. This fourth quarterly report covers activities performed during the three months of April, May, and June, 1977.

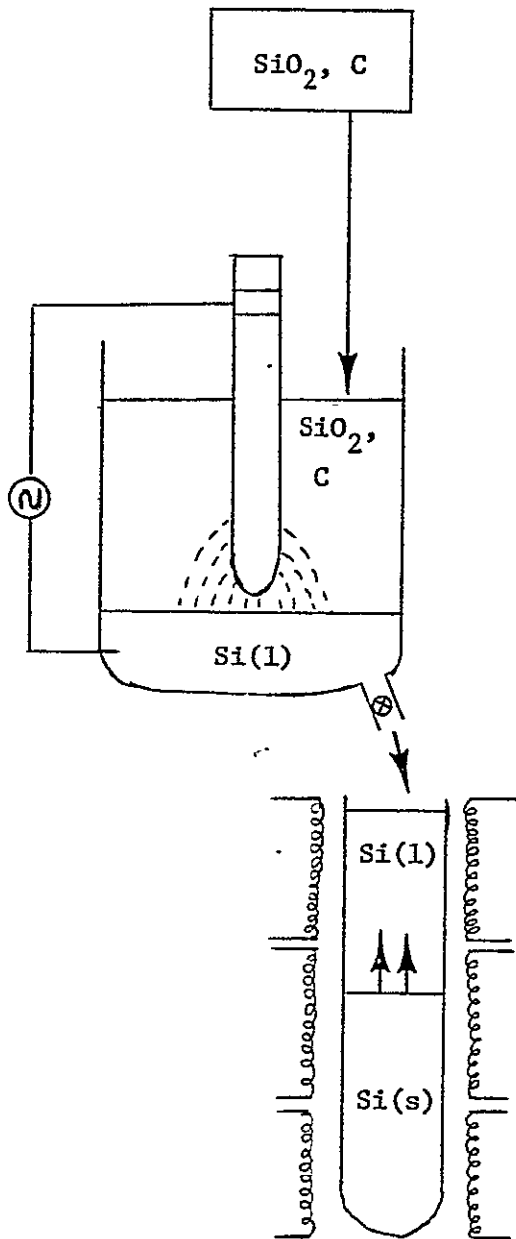
The objective of this program is to demonstrate the feasibility of a process for the production of solar-cell-grade silicon. This process should have high probability of producing silicon for sale at less than \$10/kg when scaled to 3000 metric tons per year by, or before, 1986.

The foundation upon which the major share of this program is based is 25 months of pre-JPL-contract investigations directed toward finding a high-volume, low-cost, quickly commercializable process for producing solar-grade silicon (SoG-Si). The feasibility of over two hundred possible methods for preparing silicon was determined by subjecting them to thermodynamic, economic and technological criteria. One method emerged as having a high probability of meeting the ERDA-established volume, cost, and time goals: upgrading the submerged-electrode, arc furnace process for producing metallurgical-grade silicon (MG-Si). Solar cells which had been fabricated from purified MG-Si were found to have 8-12% conversion efficiencies at air mass zero. The results of these investigations were comprehensively summarized in Quarterly Report No. 1 (1).

The overall program approach for this contract is to improve and expand upon today's technology for producing MG-Si since this material is commercially produced in electric arc furnaces at an estimated USA rate of 200,000 tons per year (500,000 globally) and sells at an average price of \$1/kg. The major goal of using improved and expanded technology, then, is to increase the purity of the MG-Si (98-% Si) to solar-grade quality while not increasing the price of MG-Si by more than an order of magnitude.

The task areas directed at improving and expanding the technology of MG-Si manufacturing are diagrammatically presented in Fig. 1. Task A is aimed at reducing the level of impurities in the raw materials so that the major portion of the impurities never actually enter the arc furnace process. This is to be accomplished by use of higher-than-normal purity raw materials. An extensive survey of quartz and quartzite

PROGRAM TASKS



- A. Purer Quartz(ite) and Carbon Raw Materials
- B. Improved Arc Furnace Materials, Construction, and Operation
 $\text{SiO}_2 + 2\text{C} \rightarrow \text{Si} + 2\text{CO}$
- C. Vacuum Evaporation (not illustrated)
- D. Unidirectional Solidification

Figure 1. Schematic Diagram Depicting Tasks for Improved and Expanded MG-Si Technology.

sources has indicated that large quantities of these materials are available at reasonable cost and with sufficient purity (2).

Charcoal, commercially used as a reductant for quartz in Brazil, has been shown to be of higher purity in most trace elements than commercial reductants commonly used today in the USA (3). It was further demonstrated that charcoal can be easily purified to reduce impurity levels below the detection limits of emission spectroscopy, i.e., about 10 ppmw (3).

Task B is concerned with the smelting of high-purity raw materials to produce high-quality arc-furnace silicon. This is to be accomplished through use of improved operating parameters, materials of construction, and furnace design. Task B also involves preventing contamination of raw materials before they enter the furnace and of molten silicon when it exits the furnace. The feasibility of smelting high-purity quartz with commercial charcoal has been established (3). The produced silicon was purer than MG-Si in all analyzed elements except for Ca and P which occur at relatively high levels in commercial charcoal. The Ca and P impurity levels can be significantly reduced through purification of the charcoal.

Task C efforts were directed at enhancing the purity of MG-Si through application of a technique not required in present-day MG-Si processing. It was demonstrated that selective volatilization of impurity elements from molten MG-Si under reduced pressure did not occur even for layers of silicon <0.1-cm thick (3). Work on this task was discontinued with JPL approval.

Impurities still existing in arc-furnace silicon that has been subjected to the first three tasks should be at a level of 1-2 orders-of-magnitude lower than that in MG-Si. Task D involves final purification via unidirectional solidification using either a Czochralski or Bridgman-type technique to effectively segregate most impurities from the solid into the melt. It is this unidirectionally solidified material that would be supplied to the Large Area Silicon Sheet Task. Purification via the Bridgman-type process has been demonstrated (2); further studies are required to determine the effects of solidification method and its rate on purification effectiveness and cost. The Czochralski process has been used to purify arc-furnace silicon produced in Task B.

A 0.08 ohm-cm (boron) polycrystalline ingot pulled from such material was analyzed at the 65%-of-the-melt-pulled point by spark-source mass spectroscopy and found to have transition metal impurities below their limits of detection of approximately 1 ppbw or less (2). Boron and phosphorus (10 ppmw) levels, however, must be further reduced through efforts in Tasks A and B.

The 65-% material from Task D was evaluated as solar cells using in-house efforts. Single-crystal material (ca. 60-% yield) was produced using both float-zoning and Czochralski techniques and was supplied to Spectrolab for fabrication into cells. Conversion efficiencies at AM0 averaged 8% for the Czochralski material and 11% for the float-zone material. Standard cells processed at the same time showed 13% efficiencies. Further improvements are anticipated when boron levels are reduced through efforts in Task A.

The next section of this report details the goals, experimental approach and progress to date in the various task areas.

III. TECHNICAL DISCUSSION

A. Task A - Raw Materials Identification and Selection

Current arc-furnace raw materials for commercially producing MG-Si are quartzite, coal, coke, and wood chips. The carbonaceous materials have been shown, in past quarterly reports, to contribute the major share of impurities to MG-Si. It is the goal of this task to find a higher-purity replacement, such as charcoal, for the carbonaceous reductants. Once a higher-purity reductant is identified, quartzite could become a major source of impurities such as Al, B, Fe, and/or P. Therefore, purer sources of quartz and quartzite are also being sought as the silicon source material.

1. Carbon Reductant

a. Charcoal Purity

Charcoal purification was further pursued this quarter using high-temperature halogen and vacuum treatments. Bark-free charcoal was used due to its higher purity.

Data reported earlier showed the effect of fluorocarbon treatment at 2000 and 2500 °C on bark-free charcoal by Ultracarbon, Inc. (2). Further data reported below in Table 1 show the results of fluorocarbon treatment at 1700, 2000, and 2500 °C using the technology of Great Lakes Research Corporation. Analyses for Al, Cr, Cu, Fe, Ni, Ti, V, and Zr are not indicated since, in all cases, their levels were below the

Table 1. Analysis of Bark-free Charcoal Purified by
Fluorocarbon Treatment at Various Temperatures

Impurity (ppmw)	Purification Temperature (°C)			
	None	1700	2000	2500
B	24	7	11	<5
Ca	3700	1000	160	50
Mg	270	<5	<5	<5
Mn	100	<10	<10	<10
P	270	90	70	<10

detection limit of at least 10 ppmw by emission spectroscopy. The data show that Mg and Mn removal is possible at any of the temperatures used. Calcium, even at the 0.1% level, is not troublesome due to its easy removal during later processing steps (2). Partial boron removal is possible at 1700 and 2000 °C whereas significant reduction occurs only at higher temperatures. Phosphorus follows a very similar trend.

The effect of high-temperature vacuum treatment on various charcoal samples was carried out by subjecting the samples to 1900 °C under a vacuum of about 0.1 Torr for four hours. The first sample was untreated bark-free charcoal, whereas the second two had been fluorocarbon treated at 1500 and 2000 °C, respectively. Data are presented in Table 2 only for elements that appeared above their detection limits by emission

Table 2. Analysis of Bark-free Charcoal Vacuum Treated at 0.1 Torr for 4h at 1900 °C

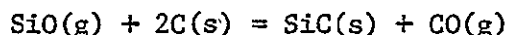
Imp- urity (ppmw)	Pre-Fluorocarbon Treatment Temperature (°C)		
	None	1500	2000
B	26	22	<5
Ca	1100	230	50
P	90	<10	<10

spectroscopy. Boron reduction to its detection limit occurs at about 2000 °C whereas phosphorus can be lowered to its detection limit at 1500 °C.

All conclusions derived from the analyses described above via emission spectroscopy must be made knowing the error associated with the analytical technique. The precision of this analytical technique has been discussed previously (2) and is treated further in a later section. In general, exact knowledge of the level of boron and phosphorus level at the 1-10 ppmw level becomes very important for making decisions regarding this contract. However, it is in this exact range that the detection limits of these elements via emission spectroscopy are reached, and consequently, that their analytical precision becomes worst. This makes clear-cut decisions very difficult to make.

b. Charcoal Reactivity

Preliminary analyses were made in an attempt to determine the reactivity of purified charcoal before using it in experiments as described later under Task B. Samples of untreated charcoal and 2500-°C freon purified charcoal were tested at SINTEF in Trondheim, Norway using a recently reported method (4). Both samples were reacted by SINTEF with a SiO/CO mixture and measurements indicated them to have the high reactivity normally associated with charcoals. The 2500-°C purified charcoal was classified as somewhat less reactive than the untreated charcoal, but it was still considered to be a highly reactive reductant. The silicon carbide produced during the measurement from the reaction



could be easily disintegrated, whereas the SiC from untreated charcoal has greater structural rigidity. This rigidity relates to the stability of the cavity (reaction zone) formed around the electrode during smelting. That is, a poor smelting is indicative of a poor cavity which, in turn, may relate back to the silicon carbide in the cavity.

Smelting experiments with high-temperature purified charcoal gave difficulties as further explained under Task B. The charcoal was further examined to determine if it were responsible for this problem. Charcoal is converted at high temperatures to graphite, a most unreactive form of carbon in an arc furnace. The degree of conversion is related in an unclear manner to time and temperature.

In order to characterize the high-temperature freon-purified charcoal, four samples purified at different temperatures were studied by X-ray diffraction. This was carried out using a copper tube with a nickel filter. The X-ray diffraction peaks are plotted at a Bragg angle of '2θ' in Fig. 3. Samples 2, 3, and 4 were freon purified at 1500, 2000, and 2500 °C, respectively; Sample No. 1 was untreated charcoal. No peak corresponding to the graphitic form of carbon was recorded in Sample No. 1. Assuming 100 % for the degree of graphitization of 2500-°C-purified charcoal, graphitization at 2000 °C and 1500 °C was observed to be 70 % and 40 %, respectively. Experimental results reported under

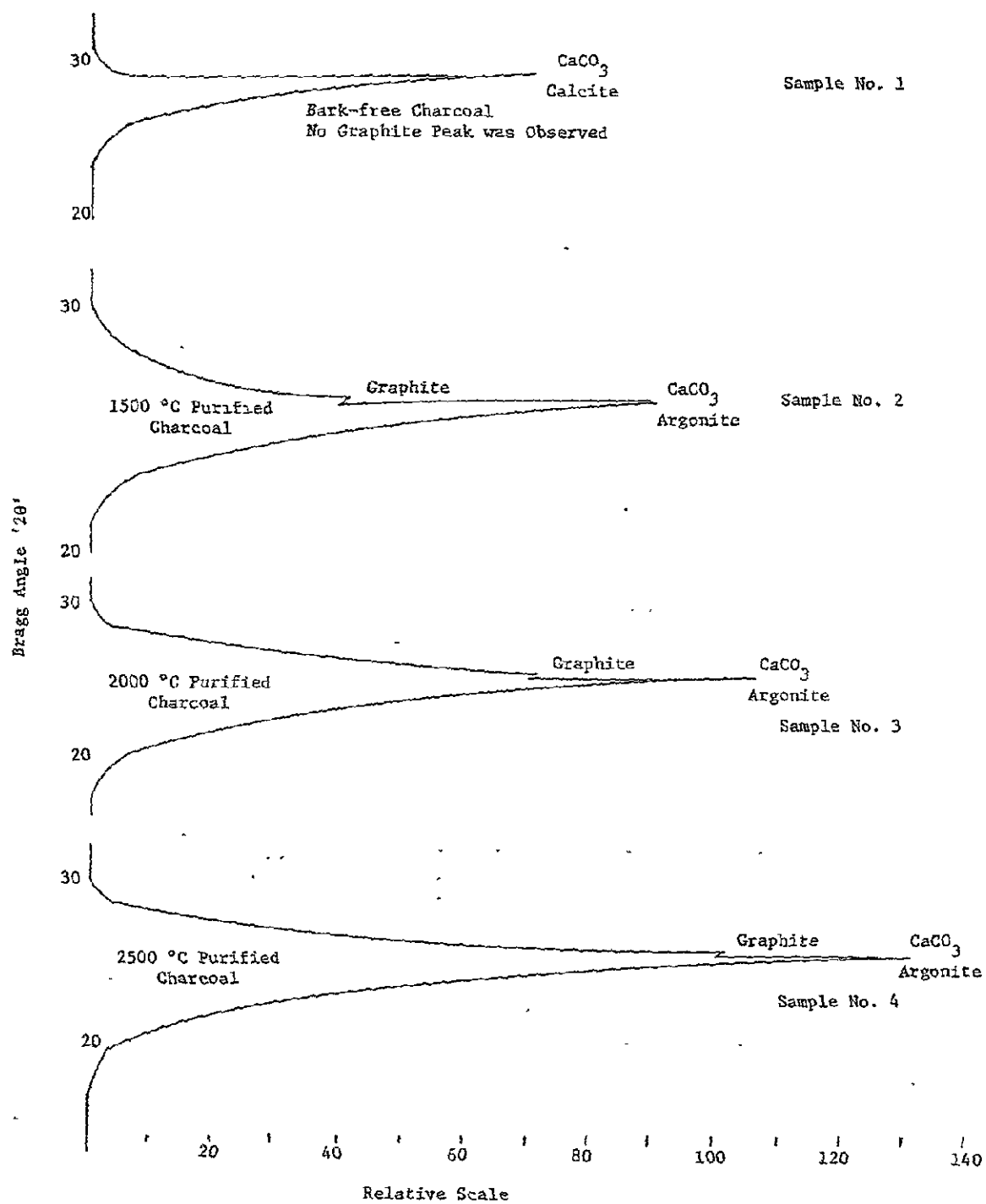


Fig. 3. X-ray Diffraction Peaks for Graphite in Charcoal Purified at Various Temperatures

Task B indicate that melting with 2500-°C-purified charcoal produced practically no silicon, whereas with 2000-°C-purified charcoal, the silicon yield was below 50 %.

One may conclude from Fig. 3 that the degree of graphitization is a function of purification temperature. The time required to bring the charcoal up to temperature, holding time at the elevated temperature, and the cool-down time are also related to graphitization.

2. Quartz and Quartzite

Quartz and quartzite sources are being examined as to location and accessibility, representative chemical composition, and estimated commercial price. Dow Corning is being assisted by Interlake, Inc, in these studies due to their experience in raw material procurement as a major MG-Si producer (5).. Physical testing of promising materials continue to be made through decrepitation studies.

A survey of domestic and foreign sources of quartz(ite) is nearly complete as far as meeting the early goals of this contract. A more in-depth survey will be required if a decision should be made to use this process to produce large quantities of silicon for the solar-cell market.

Over 90 domestic and foreign sources of quartz(ite) have been surveyed. Importers are currently supplying high-purity quartz to U. S. quartz crystal growers. This material cost is too expensive to serve as a raw material for solar-grade silicon. Crystal growers are learning, however, that milky quartz is as pure as large clear crystals. Canadian quartz is available at a reasonable cost, purity and accessibility. Combined Canadian and United States estimated reserves are sufficient for many years.

Samples were received from 36 domestic and foreign sources. Many samples were analyzed for boron and phosphorus and sometimes aluminum and iron. Samples of quartz varied and included clear crystals, semi-clear, milky, sugar texture, quartzite rock and bull quartz (from the field). The semiclear, milky and sugar texture quartz all had low boron, <1 to 2 ppmw, comparable with clear quartz crystals.

In the United States the best quartz can be obtained from Arkansas where a large number of veins break the surface from a general belt of

quartz that measures 130 km wide and up to 300 km long. Quartz of good quality, 1 ppm of boron and <10 ppm of phosphorus, and in sufficient quantities can be obtained from Malvern Minerals Company, Malvern, Arkansas and Quartz Processing Corporation, Hot Springs, Arkansas for 15-24¢/kg. Two more good sources would be Bond Optics in Lebanon, New Hampshire and Donald C. Holand, Fargo, North Dakota. Bond Optics has 2×10^6 Mt of reserves at 48¢/kg. Mr. Holand's deposit has not been mined, and reserves are being determined. There are many deposits in the western states that have not been explored or mined. If the economic need, price, and quantity increase, these can be mined.

Transportation charges and the cost of quartz is too high from Brazil and other foreign sources except Canada. Comet Quartz Ltd. Ontario, Canada and Mount Rose Mining Co. Ltd. North Vancouver, B.C. both have quartz with 1 ppm of boron and 5-9 ppm of phosphorus. Comet Quartz Ltd. has offered to supply high-grade quartz for 20¢/kg and Mount Rose Mining for 66¢/kg in small quantities. Mount Rose Mining has 80,000 Mt of proven reserves while Comet Quartz deposits are estimated at as high as 1×10^8 Mt.

Table A1 (in Appendix A), Contacts for Foreign Sources of High-Purity Quartz and Quartzite, and Table A2, Contacts for Domestic Sources of High-Purity Quartz and Quartzite, list all the contacts made during this investigation. Appendix B lists books, pamphlets, maps, and reports obtained through the search for high-purity quartz.

National Spectrographic Laboratories, Inc. performed analyses of the quartz samples.

B. Task B - Arc Furnace Studies

Commercial-Scale Material Balance

a. Purpose

A material balance was performed on a commercial-scale furnace in order to determine particularly what fraction of impurities entering the furnace as raw materials exit the furnace dissolved in MG-Si. Even though the material balance for some impurities were reported on in past publications (6-8), crucial experimental details were not provided. In addition, the current material balance considers many impurities of interest in SoG-Si as compared to earlier balances. An equally important reason for performing a detailed material balance is to provide guidance for studies in experimental-scale facilities.

b. Experimental Procedure

The material balance was performed over a 5-day period by Interlake, Inc. at the Beverly, Ohio facilities of their Globe Metallurgical Division. The furnace was approximately 9'm in diameter and 3'm deep. The 30-MVA power supply provided energy through three 130-cm graphite electrodes.

Much of the following information is excerpted from a report supplied to Dow Corning by Interlake under this contract (9).

The raw materials were sampled at the site near the bucket elevator conveying the raw materials to the storage bins. The bins were almost emptied before the test was started in order to avoid interference of unmonitored charge materials on the material balance. During the test period, a 20-40 liter representative sample of material was taken from every truck or railroad car that was unloaded to the elevator pit and samples of each material were accumulated separately. Samples collected during the week amounted to about 300 l of Alabama gravel, 300 l of North Carolina gravel, 200 l of Imperial coal, 200 l of Sewell coal, 150 l of petroleum coke and 1000 l of woodchips. Each composite sample then was riffled to a handable size for chemical analysis. Since samples of the electrodes were not taken, typical analyses for electrodes were used in the material-balance calculations.

Furnace-spout samples were taken three times per tap and composited daily. Samples of the spout sand were also taken once per shift. The fume was sampled per normal procedure and the multiclone material was sampled twice per shift and composited for the week. The ladle slag and skull were accumulated for the week, then crushed and riffled. The metal product was sampled per normal procedure each tap and composited daily.

Weights of the raw materials charged to the furnace during the test period were taken from the "Furnace Sheets" and corrected for bin scale deviations. Dry weights and carbon contents of the carbonaceous raw materials were calculated from the "Daily Natural Fixed Carbon" analysis sheets. Weights of the electrodes were calculated using the typical densities (23.8 kg/cm for the Italian electrodes and 24.5 kg/cm for the Union Carbide electrodes) and the length of the electrode consumed per the furnace sheets. Extraneous weights of objects coming in contact with the metal, such as, spout sand, silica flour, mold wash, crack filler, taphole plugs, etc., were estimated during the operation.

Skull weights were recorded when the ladle was cleaned. Actual skull weights were calculated from the ladle's previous weight and its empty weight before cleaning. Slag weight was recorded when the slag pot was emptied and the back-up ladle material was weighed when it was emptied. Since the ladle was not weighed after the silicon metal was tapped into it, furnace spout metal output was calculated by adding the metal production, actual skull and the metal in the back up ladle. Metal in the back-up ladle was calculated by subtracting the spout sand used from the total back-up material weight.

Fume and multiclone outputs were not weighed during the test period, however, values that were available for the previous week were used in calculations. The volatile matter input from the carbonaceous materials was calculated by balancing the ash and carbon with the dry weight.

Table C1 (in Appendix C) shows the daily input to the furnace as well as the daily materials used in the ladle (which initially receives the tapped MG-Si) and in the mold (where the MG-Si is cast). The moisture content and carbon content of the carbonaceous materials appear in Tables C2 and C3. The daily furnace output is given in Table C4 where

the weight of silicon in the skull and ladle are added to that in the mold to obtain the total weight of produced silicon. The daily data presented above are more clearly seen on a weekly basis in Table C5 where the weight of carbonaceous materials have not been adjusted for moisture content.

A material balance was made by using the weight data presented above along with detailed elemental analyses (not presented here due to their large number). The total weekly weight of each elemental impurity entering and leaving the furnace are provided in Table C6. Two output weights are given: one before oxygen refining (output at spout) and the other after refining (output at mold).

c. Results and Discussion

The two significant results that arise from the above material balance are (a) the distribution of impurities by raw material entering the arc furnace and (b) the fraction of each impurity that exits the furnace dissolved in the MG-Si, i.e., the recovery. This information is presented in Table 4. Impurity distribution data is further condensed for clarity in Table 5 where each impurity distribution is broken down into its silica and carbon components; the carbon component is further subdivided into coal, wood chips, and coke. The conclusions are as follows:

- Carbon is the major contributor of each impurity, except copper.
- Of the carbonaceous raw materials, coal is the major contributor of the remaining impurities, except for Ca from wood chips and V from petroleum coke.

These conclusions indicate that replacement of the normal carbonaceous reductants by a high-purity reductant, such as charcoal, is a significant factor for producing higher-purity arc-furnace silicon. Also indicated is the need of using a higher-purity silica source if a sufficiently pure reductant can be identified.

The impurity recovery data before oxygen refining are fairly consistent with those reported by Wise (6) and by Dubrous and Serptier (8). The recovery data by Fairchild (7) agrees with our data in Table 4 only when one assumes that their analyses were made on MG-Si after oxygen refining. This purification method is effective for reducing the

Table 4. Percentage Impurities Contributed by Raw Materials
and Impurity Recovery in Metal

	Al	B	Ca	Cr	Cu	Fe	P	Ti	V
Alabama Gravel	9.2	3.9	0.7	11.8	37.2	12.9	12.3	10.4	7.1
N.C. Gravel	9.8	3.9	0.7	11.4	29.9	9.7	8.0	12.3	7.1
Imperial Coal	32.4	37.1	2.4	21.7	13.6	21.3	22.6	38.0	2.6
Sewell Coal	37.1	44.1	4.6	26.9	9.9	34.1	24.7	30.0	2.6
Pet Coke	0.8	0.7	0.3	18.6	1.4	3.1	9.9	3.5	72.8
Wood Chips	6.0	5.7	88.5	9.6	8.0	14.3	21.3	5.8	7.8
Electrodes	4.7	4.6	2.8	---	---	4.6	1.2	---	---
TOTAL	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
% Recovery at Spout	80	66	50	67	73	80	14	82	95
% Recovery after Oxygen Refining	44	66	5	67	73	83*	14	77	95

* Iron pickup occurred from molds.

Table 5. Impurity Distribution According to Silica and Carbon in MG-Si from a Commercial-Scale Arc Furnace

Imp- urity	Distribution (%)				
	SiO ₂	Carbon*			
		Total	Coal	W.C.	Coke
Al	19	81	69	6	1
B	9	92	81	6	1
Ca	1	99	7	89	0
Cr	23	77	49	10	19
Cu	67	33	24	8	1
Fe	22	78	55	14	3
P	20	80	47	21	10
Ti	23	77	68	6	4
V	14	86	5	8	73

*Maximum contribution for the electrode is 5%.

concentration of aluminum by one half and the level of calcium by one order of magnitude compared to their normal values in MG-Si. The silicon recovery was 77%.

A plot of impurity recovery, before oxygen refining, versus the vapor pressure (10) of the impurity at 1650 °C appears in Fig. 2. The data trend suggests that decreased recovery is due to more highly volatile impurities vaporizing from the furnace. No reason is evident for the "nonideal" behavior of boron. The solar-cell-degrading impurity zirconium has a boiling point higher than that of vanadium and would be expected to have a recovery of greater than 95%.

2. Experimental-Scale Studies

a. Purpose

The primary goal of this task is to evaluate higher-than-normal-purity raw materials in a developmental-size arc furnace located at Elkem-Spigerverket A/S in Kristiansand, Norway. The evaluation is to determine the extent to which the silicon produced in the furnace is purified compared to MG-Si due to the use of improved raw materials. Secondary goals are to (a) become intimately familiar with the operation of the small-scale 40-kW furnace, and as of a result of this, to (b) make furnace modifications so as to improve the probability of producing higher-purity silicon, and to (c) determine and use furnace and related operating conditions suitable for the overall goal of this contract.

The primary goal of producing purer arc-furnace silicon through use of higher-quality raw materials can be quantified somewhat. Boron must be removed at the raw material step since only a small percentage is removed during smelting and solidifying. Commercial MG-Si has a boron concentration of about 22 ppmw (0.03 ohm-cm). Solar cells are reported to peak in electrical output efficiency in the range of 0.1-0.5 ohm-cm (11-14). Therefore, it is our goal to reduce the level of boron in silicon from 22 to 0.7 ppmw, corresponding to an increase in resistivity from 0.03-0.3 ohm-cm. Results below show that about half of this goal has been reached through production of 0.091 ohm-cm (4 ppmw of boron) material after only seven experiments in the 40-kW furnace in Norway.

Two earlier experiments demonstrated the feasibility of smelting quartz and commercial charcoal in an arc furnace (3). The same furnace

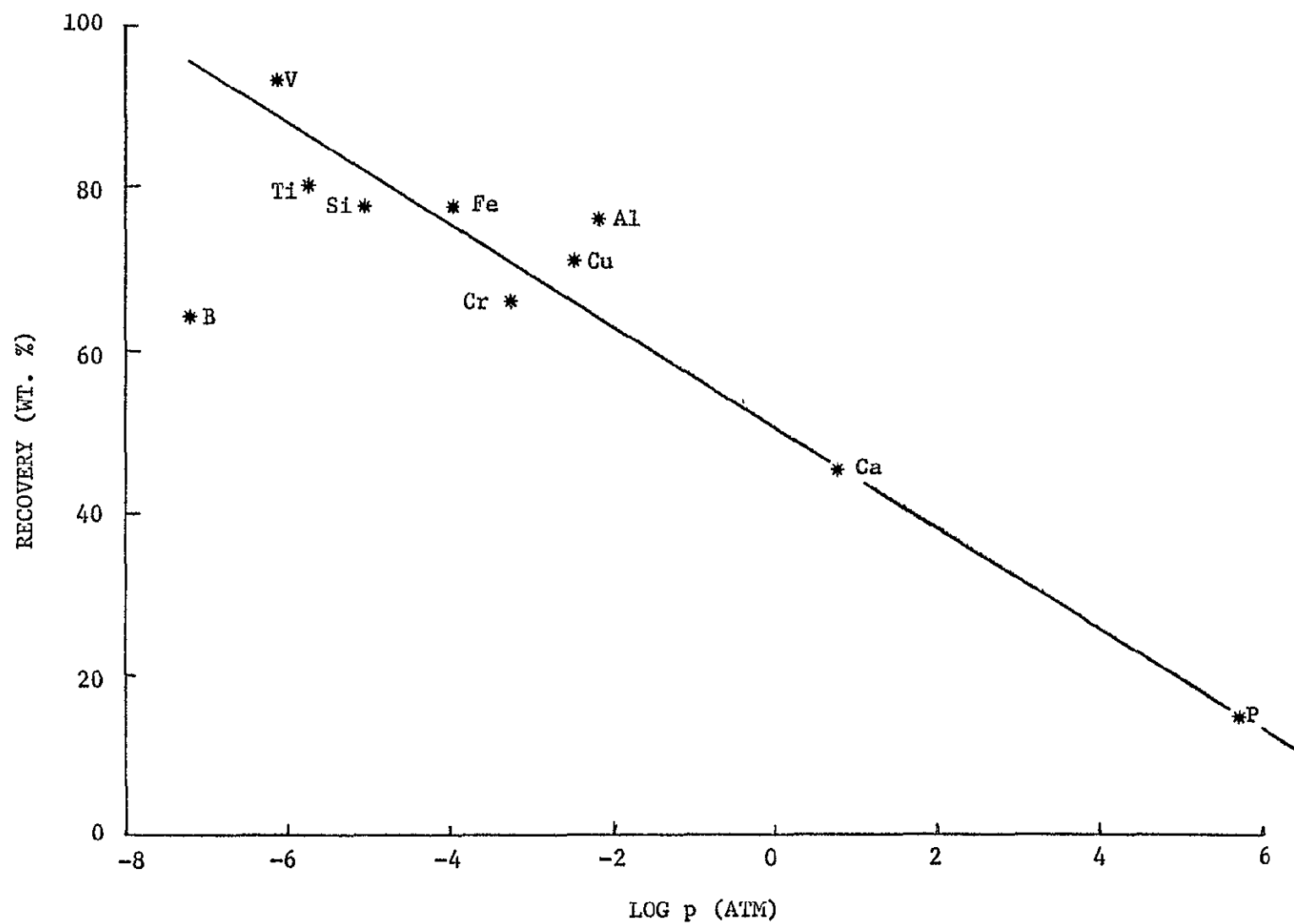


Figure 2. Impurity Recovery as a Function of Elemental Vapor Pressure at 1650 °C.

was used to perform four additional experiments using higher-purity quartz and various grades of purified charcoal. The furnace is shown in Fig. 3 with the electrode extending into the top of the upper smelting chamber (44 cm in height). A SiC-coated graphite tapping spout exits from the bottom chamber. Silicon metal is tapped into the quartz crucible below the tapping spout.

b. Experimental Procedure

For reference purpose, the four experiments are described below in Table 6 in terms of the raw materials used. All quartz was from Arkansas and differed in opacity and source location. The main difference in the charcoal was the temperature at which it was purified by freon-treatment.

Table 6. Raw Materials Used in Arc-Furnace Experiments

Exper. No.	Quartz (Arkansas)	Charcoal
4	Milky, Garland County	Regular, freon-treated at 2500 °C
5	Milky, Saline County	Bark-free freon-treated at 2000 °C
6	Semiclear	Bark-free, untreated
7	Semiclear (18 h) and Milky, Saline Co. (9 h)	50% Bark-free, untreated + 50% Bark-free, freon-treated at 2000 °C

Quartz shipped to Norway was crushed to size in Elkem facilities. Analyses of samples before and after crushing showed the quartz to have been severely contaminated with aluminum. Analyses which were previously in the 20-100 ppmw range increased to about 1000 ppmw (0.1%). Charcoal and electrode samples were used as shipped with no contamination problem resulting. Average raw material analyses appear in Table 7 for quartz, charcoal, and graphite electrodes. At significant increases above their detection limits, only aluminum appears in quartz, Al, Ca, Fe, and P are in charcoal, and only Fe is detected in the electrodes. All quartz samples passed the Elkem decrepitation tests. Charcoal analyses for moisture, volatiles, ash, and fixed carbon are given in Table 8. High-temperature purified charcoal approaches 100% carbon.

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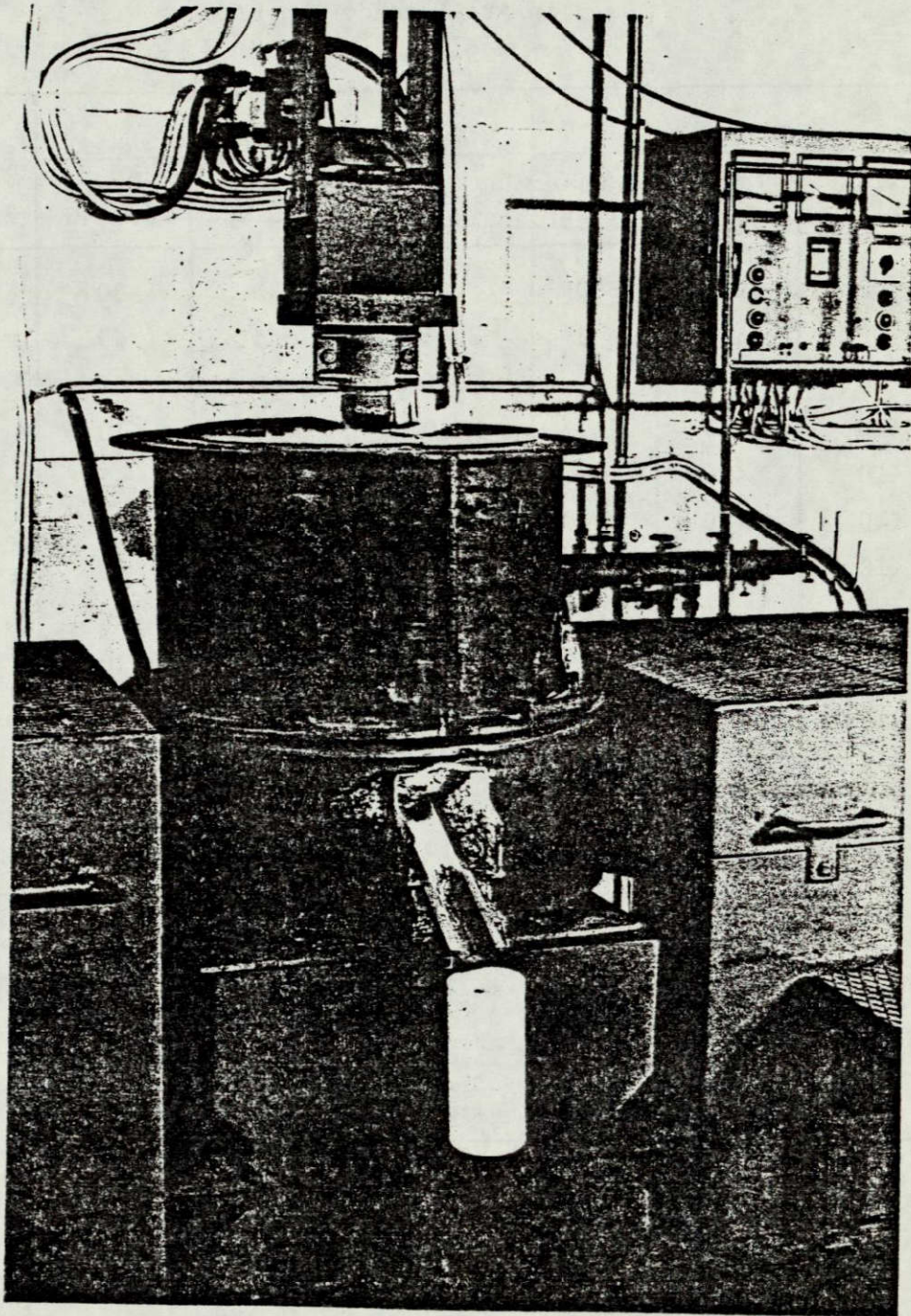


Fig. 3. Photograph of 40-kW Arc Furnace
Used at Elkem-Spigerverket

Table 7. Impurity Analyses of Raw Materials
Used in Arc-Furnace Experiments

Imp- urity (ppmw)	Quartz			Charcoal			Elect- rode 2500 °C
	Milky Garland	Milky Saline	Semi Clear	Untreat- ed	2000 °C	2500 °C	
Al	1400	1200	860	<10	30	30	<10
B	5	3	3	<5	<5	<5	<5
Ca	<10	10	<10	3600	40	60	<10
Cr	<10	<10	<10	<10	<10	<10	<10
Cu	<10	<10	<10	<5	<5	<5	10
Fe	<10	10	<10	10	40	30	40
Mg	<10	10	<10	200	<5	<5	<10
Mn	<10	<10	<10	70	<10	<10	<10
Ni	<10	<10	<10	<10	<10	<10	<10
P	<10	10	<10	60	30	20	<10
Ti	<10	<10	<10	<10	<10	<10	<10
V	<10	<10	<10	<10	<10	<10	<10
Zr	<10	<10	<10	<10	<10	<10	<10

Table 8. Charcoal Analyses for Arc-Furnace Experiments

Charcoal Purification	Moisture (%)	Volatiles (%)	Ash (%)	Carbon (%)
None	2.5	11.9	3.2	82.5
2000 °C	0	0.4	0	99.5
2500 °C	0	0.4	0	99.6

Several arc-furnace modifications were made with the goal of assuring higher-purity smelting conditions. Reference to furnace diagrams in Quarterly Report No. 2 will aid in understanding the following modifications (3).

- A quartz liner was placed internally adjacent to the ceramic liner to minimize contamination from the ceramic.
- A graphite lid was placed on top of the furnace to prevent condensed material on the electrode holder from falling back into the furnace.
- The bottom hearth was spectrographic-grade graphite.
- Stoking was done with graphite rods.
- The tapping spout was SiC-coated graphite.

Smelting experiments were conducted very similarly to that described earlier (3). Comparable data for each arc-furnace experiment is given in Table 9.

Table 9. Various Data for Arc-Furnace Experiments

	Experiment No.			
	4	5	6	7
Quartz (kg)	56	84	103	110
Charcoal (kg)	21	29	38	38
Electrode (kg)	0	4	6	6
Time (h)	15	30	30	27
Silicon Out (kg)	0.3	4	15	12
Energy (kWh/kg)	-	188	60	56

c. Smelting Results and Discussion

Presented below is a description of each experiment followed by a general discussion of the smelting characteristics (18).

Smelting Test No. 4

Raw Materials: Quartz, Milky White (Garland Co.)
Charcoal purified at 2500 °C

The carbon content of the charge was 100% (100% carbon content is defined as 2C per SiO_2). The furnace operation was quite smooth most of the time with a fairly constant current, but in periods the resistance was unstable and it was difficult to find an electrode position where the load was acceptable. Gradually, a cavity formed around the electrode, but it was much smaller than normal for silicon smelting, and the furnace content appeared more porous than normal at the top.

No metal came at the tapplings, and it was thought that too much of the Si was bound as SiC. Therefore, excess SiO_2 was added. Still, no metal was tapped.

The formation of silicon carbide was apparent when the electrode had to be changed. Then a large lump of silicon carbide stuck to the electrode when it was withdrawn. The electrode penetrated into the lump where it formed a small cavity. Since the electrode tip was conical, an arc might have been formed between the electrode and the lump almost everywhere on the lower part of the electrode, and the lump may have conducted current to the bottom of the furnace.

Shortly after the change of electrode, the operation had to be broken off because of difficulties with the hydraulic regulation system. At the excavation, it was found that the furnace contained very much silicon carbide. The charcoal particles were converted to silicon carbide with the tree structure preserved. This structure was fairly porous, but the pores were filled with metal giving the particles a metallic appearance.

Smelting Test No. 5

Raw Materials: Quartz, Milky White (Saline Co.)
Charcoal Purified at 2000 °C

Smelting was very easy using a charge with a carbon content of 94%. Since metal production was low, the carbon content was reduced to 86% and quartz was added directly to the cavity during stoking. Even though silicon production improved towards the end of the test, furnace resistance became rather unstable.

At the excavation, a fairly large cavity was found around the electrode tip. It contained much quartz and silicon carbide.

Smelting Test No. 6

Raw Materials: Quartz, Semiclear
Regular Charcoal, Untreated

The carbon content was initially 100% but was soon decreased to 96% and later to 90 and 88%. In addition, some quartz was added directly into the crater after the stokings. A large cavity formed readily, and stoking and tapping was easy. Fairly large amounts of metal were produced.

The excavation showed a large cavity, but there was a considerable amount of silicon carbide and metal in the bottom of the furnace. Charcoal particles in the upper part of the cavity were transformed to silicon carbide, but the pores in the particles were not filled with metal.

Smelting Test No. 7

Raw Materials: Quartz, Semiclear then Milky White
Charcoal, Unpurified (50%)
Charcoal Purified at 2000 °C (50%)

The carbon content of the charge was initially 94% but it was necessary to lower it to keep the electrode low and produce metal. During the last ten hours of smelting, the carbon content of the charge was only 80%, and some quartz was added directly into the crater after the stokings. When the estimated electrode consumption was included, the carbon content of charge plus electrode was 92%. With low carbon, the furnace resistance was periodically unstable. There was some fuming, but visually estimated, the amounts of fumes were moderate.

The excavation showed a large cavity with fairly small accumulations of silicon carbide. Some of the charcoal particles converted to silicon carbide were porous while others were completely soaked with metal.

Some general observations on smelting are made at this point.

One smelting of each charcoal type is not enough to judge if the charcoal is acceptable or not. Excess carbon will give deposits of silicon carbide even with a very reactive carbon material, and correct carbon balance is essential for good process conditions. During the smelting, the carbon balance is adjusted according to electrode movement and metal production, and the excavation shows if the resulting carbon content was correct.

The smeltings reported here are the first tests for each material, and should be considered only as indications. In the Tests No. 4 (with charcoal purified of 2000 °C) and No. 6 (with regular charcoal), the carbon content was too high judged from the excavation where large deposits of silicon carbide were found. In Test No. 7, (with a mixture of regular and purified charcoal), a balance between formation and consumption was obtained. The charging of quartz was, however, irregular, with considerable amounts of quartz charged directly into the crater after stoking. This may be necessary for the result.

In Test No. 5 (with charcoal purified at 2000 °C), both silica and carbon were found in the crater. This indicates that the reaction will be difficult even with sufficient amounts of quartz. After some more tests, however, a better combination of carbon content and voltage may be found, and the materials will perhaps be consumed completely.

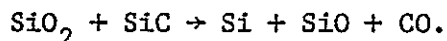
Test No. 6, with regular charcoal, gave easy operation, and silicon carbide deposits could probably have been prevented with lower carbon content of the charge. Then, all the reduced material in the hearth should be recovered as metal and the energy consumption per unit metal should be much lower. In the last test with mixed charcoal, almost all the metal produced was recovered; therefore, the potential energy consumption for regular charcoal is considerably lower than for the mixture.

In Test Nos. 4 and 5, with purified charcoals, the silicon carbide deposits might have been prevented by a lower carbon content of the charge. Then, however, the silicon recovery would be very low, and consequently the energy consumption per unit metal high. Further tests may show if such a process is possible.

Clearly, the purification treatment has lowered the suitability of charcoal for smelting of silicon metal. As shown under Task A, the treatment has a strong influence on the X-ray diffraction diagram, and this may give a simple preliminary testing procedure of the suitability of the purified charcoal.

In the excavation after tests with regular charcoal, the carbidized charcoal lumps were porous, while they were soaked with silicon in the excavations after tests with purified charcoal. Maybe the reactivity of the silicon carbide and silica have some connection with the wetting of the carbide by the metal.

The reactivity of silicon carbide is considered to be critical for producing silicon in the arc-furnace process since it takes place in the reaction



Silicon carbide exists in two forms: hexagonal or orthorhombic α -SiC and cubic β -SiC. According to the JANAF Tables (15), β -SiC transforms to α -SiC at about 2000 °C. However, this seems unlikely since both phases have been prepared over temperature ranges of 1425 - 2700 °C. Heat of formation and equilibrium data indicate that β -SiC is more stable up to 1730 °C as compared to α -SiC.

Representative samples of silicon carbide from the cave of all the four experiments were studied by X-ray diffraction. Both α -SiC and β -SiC were found in the samples from the first three tests. All three tests had excess free carbon in the charge mixture. The fourth test, with nearly correct carbon content of the charge, resulted in only β -SiC.

When smelting with excess carbon in the charge mixture, the unreacted carbon along with the silicon carbide from the cave descends to the hottest zone of the furnace, where the temperature is considered to be in excess of 2000 °C. The excess carbon in the hot zone is then converted to α -SiC. With no excess carbon present in the charge, very little or no α -SiC is formed. The α -SiC with silver-gray metallic appearance found in the bottom hearth does not react efficiently with SiO_2 and is not desirable (16). In order to obtain successful melting conditions in the future, the appropriate carbon content of the charge must be determined.

d. Purity Results and Discussion

An impurity balance was attempted on each of the four experiments based upon the ratios of and analyses of the raw materials entering the arc furnace as well as the analyses of the tapped silicon. The impurity balance data are not presented here for several reasons.

- A significant portion of the raw materials do not react during the short smelting time.
- Most impurities in the raw materials are present in concentrations less than their limits of detection.

- At low concentrations, the precision of the analytical measurement is low.

Two definite conclusions, however, could be drawn from the rough impurity balance. Aluminum was found to be 2-10 times lower in the silicon than expected from the contaminated raw materials. No clear-cut explanation is available for this observation. On the other hand, iron was about a factor of ten higher in the silicon (200 versus 20 ppmw) than would be expected. This could be due to contamination from the furnace. The next series of arc-furnace tests will attempt to reduce the iron contamination.

Emission spectroscopic analyses of tapped silicon from the four smelting tests were made by individually melting several taps from each test in a Czochralski-puller furnace in order to attain a homogeneous material. A sample was sucked up into a quartz tube and allowed to quickly solidify. The Czochralski crucible melt was maintained under vacuum for one hour and sampled again. Duplicate samples before and after vacuum treatment showed no measurable difference.

Actual analyses of silicon from the smelting tests are shown in Table 10. Also enclosed is the average analysis of commercial MG-Si.

Table 10. Emission Spectroscopic Analysis
of Silicon from Arc-Furnace Tests
Compared to Commercial MG-Si

Imp- urity (ppmw)	Commer- cial MG-Si	Smelting Test			
		4	5	6	7
Al	1300	110	420	40	110
B	11	6	8(4)*	17(13)	9(8)
Ca	250	80	50	260	210
Cr	390	<10	<10	<10	<10
Cu	60	<5	10	10	<5
Fe	4200	220	290	190	120
Mg	<5	<5	<5	10	<5
Mn	120	<10	<10	60	10
Ni	100	<10	<10	<10	<10
P	10	10	20	30	70
Ti	500	<10	20	60	20
V	230	<10	<10	<10	<10
Zr	30	<10	<10	<10	<10

*() determined by resistivity on float-zoned sample.

Little can be said about the data for Test No. 4 since a near-zero silicon yield was obtained. However, Test No. 5 with 2000-°C-purified charcoal gave the lowest boron level to date. The 4-ppmw value was obtained by the very precise electrical resistivity measurement (0.091 ohm-cm) made on a float-zoned, single-crystalline sample. This 4-ppmw level represents about the half-way point in reducing the boron level of 22 ppmw in MG-Si (average) to the 0.7 ppmw required for SoG-Si. Within the limits of the analytical data, the only other significant high levels of impurities are Ca and P in Test Nos. 6 and 7 where untreated charcoal (high Ca and P) was used as the reductant.

The analytical data for the smelting tests are better presented in Table 11 as a ratio to the impurity analyzed in the silicon from the

Table 11. Ratio of Impurity Concentration in Experimentally-Produced Si to Commercially-Produced MG-Si

Imp- urity	Experiment/Commercial Ratio			
	Test 4	Test 5	Test 6	Test 7
Al	0.08	0.3	0.03	0.08
B	0.4	0.2	0.8	0.5
Ca	0.3	0.2	1.0	0.8
Cr	<0.03	<0.03	<0.03	<0.03
Cu	<0.08	0.2	0.2	<0.08
Fe	0.05	0.07	0.05	0.03
Mg	-	-	-	-
Mn	<0.08	<0.08	0.5	0.08
Ni	<0.1	<0.1	<0.1	<0.1
P	1.0	2.0	3.0	7.0
Ti	<0.02	0.04	0.12	0.04
V	<0.04	<0.04	<0.04	<0.04
Zr	<0.3	<0.3	<0.3	<0.3

smelting test to that found in commercial MG-Si. The lower the ratio, the higher the purification due to use of better raw materials in the arc furnace. Considerable improvement is seen for all impurities, except for phosphorus where analytical measurements are near the detection limit.

Arc-furnace silicon from Tests 5, 6, and 7 was subjected to unidirectional solidification, the last purification step in the overall process being considered. Arc-furnace silicon was pulled from a Czochralski puller giving single-crystal yields of 56, 61, and 64%, respectively, for the three experiments. Higher yields are expected once sufficient quantities of arc-furnace silicon are available to optimize the solidification process. Emission spectroscopic analyses of the single-crystalline ingots showed all the impurities normally analyzed for, except boron, to be present at less than their limits of detection of 5-10 ppmw. Spark-source mass spectroscopic analysis of similar samples reported in the last quarterly report (2) showed metal impurities to be in the ppbw, or less, range implying that the silicon material should meet or exceed solar-grade silicon specifications.

C. Task C - Vacuum Evaporation Studies

This task involved the study of MG-Si purification by vaporization of volatile impurities under vacuum conditions. Work in this area was discontinued, with JPL approval, due to the lack of any evidence of MG-Si purification based upon reported data (3).

D. Task D - Unidirectional Solidification Studies

1. Czochralski-Type Technique

a. Experimental

Two ingots were grown by the Czochralski method this quarter to investigate the effectiveness of this purification technique at larger ingot diameters and higher growth rates. Ingot diameters of 70 mm and 85 mm and growth rates of 50 mm/h and 90 mm/h correspond to make rates of silicon from 520 g/h to 1000 g/h. Emission spectrographic analysis has been completed. All impurities, with the exception of boron and phosphorus, were below the detection limit at the 63-percent point for the 1000 g/h pull rate and below the 76-percent point for the 520 g/h pull rate. The latter yield is probably a true limit established by the purity of the melt while the former run was terminated at the 63-percent point due to diameter control problems. Further mass spectrographic analysis is required to establish the actual purity. However, these preliminary results are promising.

b. Cost Analysis

A key process step in the proposed upgrading of MG-Si has been the use of unidirectional freezing as a purification method. Unidirectional freezing is highly effective due to the extremely small segregation coefficients of most of the impurities found in silicon. A preliminary economic analysis of the Czochralski crystal growth process as a method to effectively segregate impurities was conducted in late 1975 (17). Since that time a considerable amount of additional data has been developed relating to the growth of large-diameter ingots (16-20 cm), crystal structure requirements to achieve effective segregation, the dependence of effective segregation on melt impurity concentration and ingot growth rate, and finally, a better understanding of the purity requirements of the purified ingot. Based on these data, the economic analysis of the Czochralski process has been refined and extended. The add-on cost for unidirectional freezing has been determined for a variety of ingot diameters (16 cm, 20 cm, and 30 cm) and corresponding crucible capacities (43 kg, 120 kg, 200 kg). Various modes of equipment operation have also been considered including:

- Continuous growth with melt replenishment,
- Sequential growth with melt replenishment and residue removal, and
- Sequential growth with melt replenishment alone (2).

A comparison of the sequential growth process with melt replenishment indicated that residue removal (crucible remains where growth is completed) is highly desirable for any system in which relatively high impurity concentrations exist in the melt. For this reason, only results for the sequential growth system with residue removal are reported.

Several assumptions have been made regarding the overall process in addition to the size of the ingot, molten silicon charge, and the modes of operation. These include:

- The ingot can be polycrystalline.
- Average impurity concentration in any ingots grown should not exceed five times the impurity concentration in the first-to-freeze material. This implies that, for the impurities of interest, only 90% of the melt can be removed in ingot form prior to residue removal and melt replenishment and, that if M_0 is the original melt mass in the continuous growth system, only $9 M_0$ can be converted to ingot form before the system must be shut down and reloaded.
- Crucible/furnace construction is such that sufficient operating time can be achieved to have the above purity requirements limit cycle times.
- Cooling water costs will be reduced to an insignificant amount through water recirculation.
- Furnaces will be operational eighty percent of the time. Twenty percent of the time is devoted to furnace cooldown at completion of a growth cycle, furnace clean-up, and maintenance.
- Power consumption will decrease as ingot diameter (and production rate) increases.
- Installed capital equipment costs are 2.5 times capital equipment costs.
- Installed capital equipment costs are depreciated over a 7-year period.

Replacement parts costs (excluding heaters and crucibles) are proportional to capital equipment costs and equal the depreciated amount on the capital equipment per year.

Equipment and process parameters used in this analysis are summarized in Table 12. Growth rates are calculated based on a realistic thermal model. This model is in good agreement with growth rates achieved at 10-cm and 12-cm diameters in existing crystal-growth furnaces, but predicted growth rates are significantly below the maximum theoretical growth rates. The characteristics of the 16-cm diameter ingot system are not significantly different from capabilities of current developmental models of crystal growth equipment with the exception of the mode of operation (sequential or continuous). Growth time is actual time during which full-diameter ingot is being produced while total cycle time includes loading time (T_L), seed/taper time (T_S), and load/reload time (T_R) for sequential load systems. The effective make rate is the product of the make rate, utilization factor (0.8) and the ratio of growth time to total cycle time. Yearly production is the product of effective make rate and 8760 hours. The capacity of these machines operating in a continuous mode or sequential mode with replenishment is substantial particularly when compared with the capacities of existing 7.5-cm and 10-cm diameter growth equipment (1000-3000 kg/y).

Labor costs are shown in Table 13. The number of operators per machine was determined by adding all labor related hours (seeding, loading, reloading) to ten percent of the hours the machine would be in the automatic growth mode and dividing by the total cycle time. The resulting numbers are considered to be extremely conservative since semiconductor production facilities normally have from 0.25 to 0.45 operators per machine. The labor rate is that used in other JPL-related economic analyses. A 100-percent overhead has been assumed. The advantage of the continuous growth process becomes apparent in this table. Labor costs for this sequential process exceed those of the continuous process by a factor of about four.

Table 14 summarizes the capital equipment costs. The capital costs represent reasonable extrapolations from current equipment costs to the somewhat larger equipment considered here. The installed cost is

Table 12. Equipment/Process Parameters

Process/Equipment Parameters \ Type Process		Sequential Growth With Melt Replenishment and Residue Removal			Continuous Growth and Melt Replenishment		
1	Ingot Diameter (cm)	16	20	30	16	20	30
2	Growth Rate (cm/h)	8	7	5	8	7	5
3	Charge Weight (kg)	42	120	200	42	120	200
4	Crucible Size h/d (cm)	25/36	32/50	40/60	25/36	32/50	40/60
5	Make Rate (kg/h)	3.75	5.12	8.23	3.75	5.12	8.23
6	Number of Ingots Grown	10	10	10	N/A	N/A	N/A
7	Growth Time (h)	100.8	210.6	218.7	100.8	210.6	218.7
8	Total Cycle Time (h)	146.8	285.6	300.7	106.8	221.6	228.7
9	Effective Make Rate* (kg/h)	2.06	3.03	4.79	2.83	3.90	6.30
10	Silicon Production ⁺ (kg/y)	18,045	26,542	41,960	24,790	34,164	55,188

* The effective make rate is the product of make rate, growth time, and utilization factor divided by the total cycle time. Utilization factor is assumed to be 0.8 with the remaining 0.2 fractional time being devoted to cool-down, clean-up, and machine maintenance.

⁺ Silicon production is the product of effective make rate and 8760 hours.

Table 13. Labor Costs

<div> <div>Process/Equipment</div> <div>Labor Related Cost Parameters</div> </div>	Sequential Growth With Melt Replenishment and Residue Removal			Continuous Growth and Melt Replenishment		
	16	20	30	16	20	30
1 Operators/Machine	0.44	0.38	0.40	0.15	0.13	0.13
2 Operator Hours/Machine/Year (h)	3,854	3,334	3,495	1,314	1,139	1,139
3 Direct Labor Cost/Machine/Year (\$) (6.90/h Labor Rate)	36,593	23,005	24,116	9,067	7,959	7,859
4 Supervisor/Maintenance Costs (\$) 0.5 x Direct Labor Costs	18,495	11,503	12,058	4,534	3,930	3,930
5 Total Direct Costs (\$)	55,090	34,508	36,274	13,601	11,789	11,789
6 Overhead Cost (\$) (100-Percent Total Direct)	55,090	34,508	36,274	13,601	11,789	11,789
7 Total Labor Costs (\$) (5 + 6)	110,180	69,016	72,548	27,202	23,578	23,578
8 Labor Cost/kg Si Produced (\$)	5.03	2.60	1.73	1.10	0.69	0.43

Table 14. Capital Costs

Process/Equipment Capital Costs	Sequential Growth With Melt Replenishment and Residue Removal			Continuous Growth and Melt Replenishment		
	16	20	30	16	20	30
1 Equipment Cost (\$1000)	175	200	250	200	250	300
2 Installed Cost (\$1000) (2.5 x Equipment Cost)	437.5	500	625	500	625	750
3 Capital Cost/kg Si(\$) 7-year Straight-Line Depreciation	3.46	2.69	1.94	2.88	2.61	2.13

considered to be 2.5 times the cost of the capital item. This 2.5 multiplier is considered reasonable since the growth equipment comes complete requiring only water, electrical, and vacuum/gas hook-up. Also since the installed cost is used for the seven-year straight-line depreciation, the dollar cost/kg Si is probably conservative.

Expendable items, power, and maintenance costs are summarized in Table 15. It has been assumed that thick-walled crucibles will be used with a life expectancy of one cycle. Heater life is assumed to be 10 cycles. Maintenance costs are high, but are consistent with the high utilization rate of this equipment when compared to existing crystal growth equipment. Power costs (Item 9) are based on a 2.5 cents/kWh rate which is currently being employed elsewhere in the JPL program.

The cost of major items is summarized in Table 16 and graphically in Figures 4 and 5. Total cost as well as each cost component are size/volume dependent as shown in Figure 4 and 5. Most significant cost reduction occurs in labor and capital as ingot diameter/melt volume increases. Little difference exists between the Continuous Growth Process and the Sequential Growth with Melt Replenishment Process except in the area of labor costs where the difference is quite significant. The fact that capital costs for the continuous growth process are less than for the sequential process reflect the fact that the make rates of the former systems are significantly higher and more than offsets the added cost of equipment.

Total cost shown in Line 6 of Table 16 indicates that several of the system configurations can achieve add-on costs well below ten dollars per kilogram. The G&A cost, and costs of the arc-furnace silicon have intentionally not been included. In Figure 6, the cost of the purified silicon is plotted as a function of net cost of arc-furnace feedstock material for the growth system considered. Regardless of the cost of the feedstock, the sequential growth of a 16-cm diameter ingot cannot achieve the \$8.70 cost goal ($\$8.70 + 15 \text{ percent G and A} = \$10/\text{kg Si cost}$). If cost of material produced by an upgraded arc-furnace process could be held to the cost of current arc-furnace silicon, the sequential growth system with a 20-cm diameter ingot could achieve the cost goal. The other four systems considered are all capable of achieving the cost

Table 15. Expendable Items/Maintenance Costs

Process/Equipment Cost Item	Sequential Growth With Melt Replenishment and Residue Removal			Continuous Growth and Melt Replenishment		
	16	20	30	16	20	30
1 Crucible (\$) (1 per cycle)	200	400	600	200	400	600
2 Heater Assembly (\$) (1 per 10 cycles)	1,000	2,000	3,000	1,000	2,000	3,000
3 Misc./Cycle (\$) (Seed, water, argon, etc.)	175	350	500	150	300	400
4 Total Expendable Cost (\$) Per Cycle	475	950	1350	450	900	1300
5 Silicon Produced/Cycle (kg)	378	1090	1800	378	1090	1800
6 Expendable Cost/kg Si (\$/kg)	1.26	0.88	0.75	1.19	0.83	0.72
7 Maintenance Costs (\$1000) (0.14 x Capital Equipment Costs)	25	28.57	35.71	28.57	35.71	42.86
8 Maintenance Costs/kg Si (\$/kg)	1.39	1.08	0.85	1.15	1.05	0.78
9 Power Costs* (\$/kg) (2.5 cents/kWh)	0.75	0.63	0.55	0.75	0.63	0.55

* Power requirements estimated as 30 kWh/kg (16-cm diameter), 25 kWh/kg (20-cm diameter), and 22 kWh/kg (30-cm diameter).

Table 16. Cost Summary

<div>Process/Equipment</div> <div>Cost Item</div>	Sequential Growth With Melt Replenishment and Residue Removal			Continuous Growth and Melt Replenishment		
	16	20	30	16	20	30
1 Capital (\$/kg Si)	3.46	2.69	2.13	2.88	2.61	1.94
2 Labor (\$/kg Si)	5.03	2.60	1.73	1.10	0.69	0.43
3 Expendables (\$/kg Si)	1.26	0.88	0.75	1.19	0.83	0.72
4 Maintenance (\$/kg Si)	1.39	1.08	0.85	1.15	1.05	0.78
5 Power (\$/kg Si)	0.75	0.63	0.55	0.75	0.63	0.55
6 Total (\$/kg Si)	11.80	7.88	6.01	7.07	5.81	4.42

Figure 4. Scale Dependence of Major Cost Items for Sequential Growth Process. (Numbers in () Indicate Ingot Diameter).

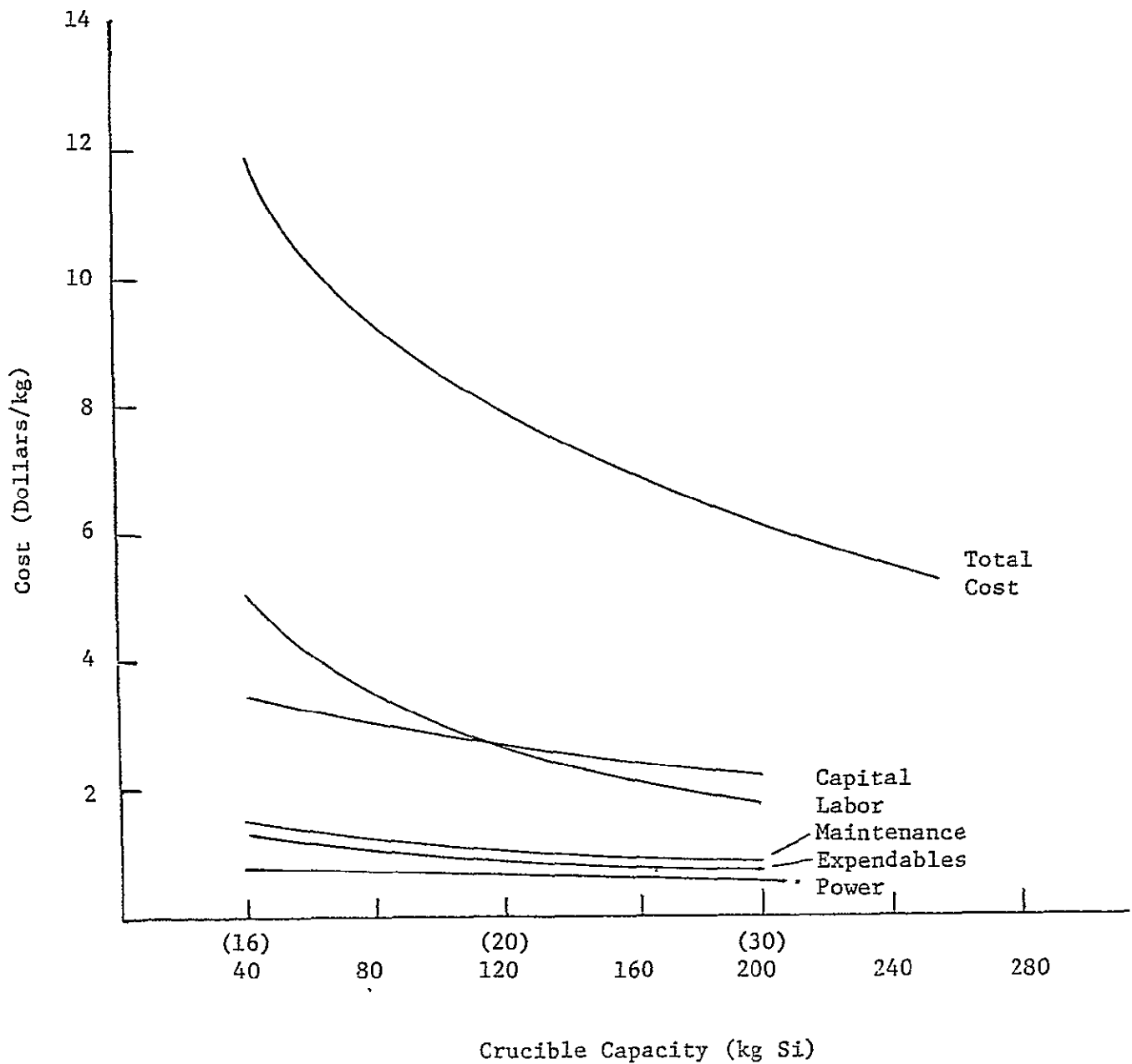
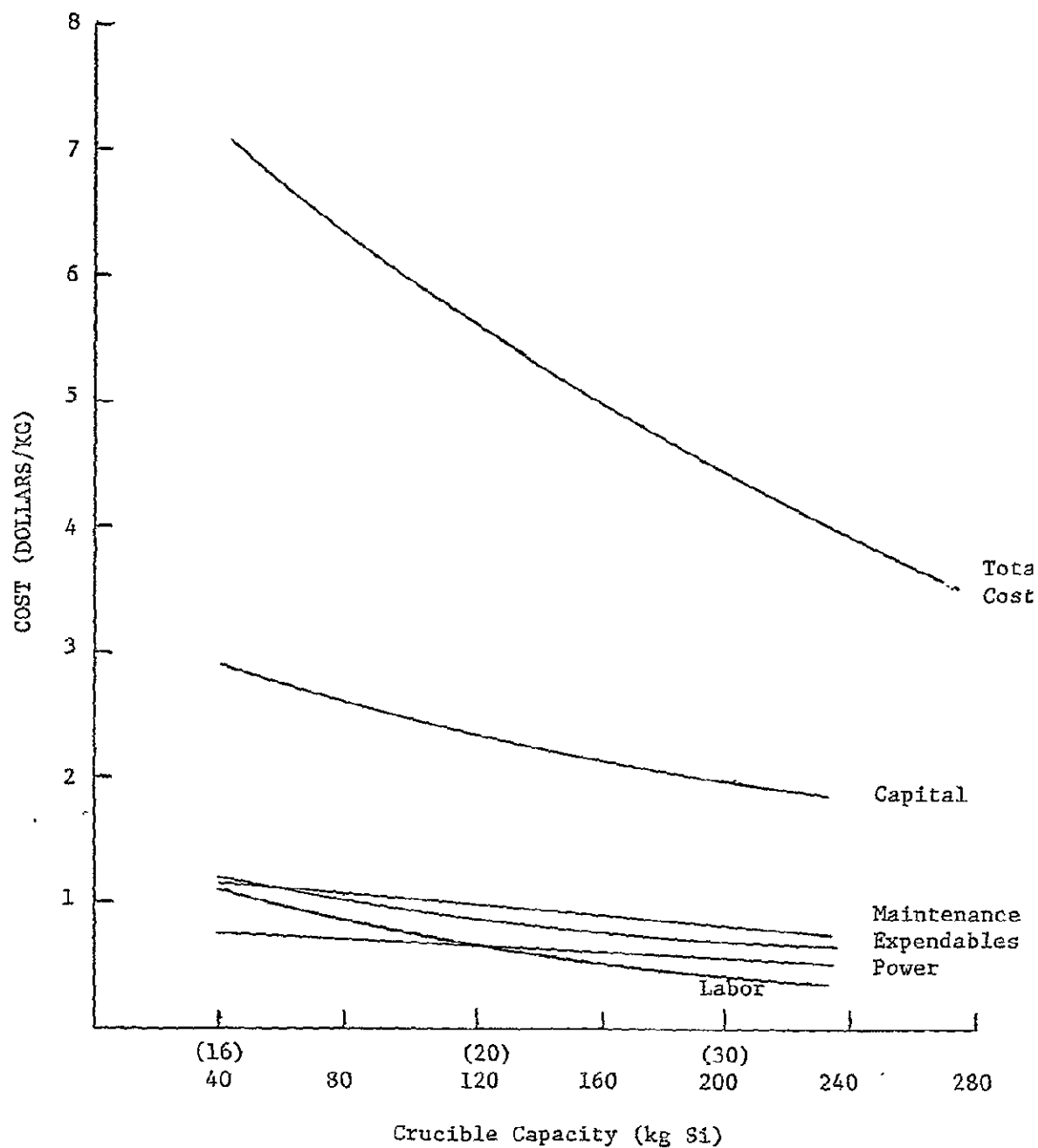


Figure 5. Scale Dependence of Major Cost Items for Continuous Growth System (Number in () Indicate Ingot Diameters)



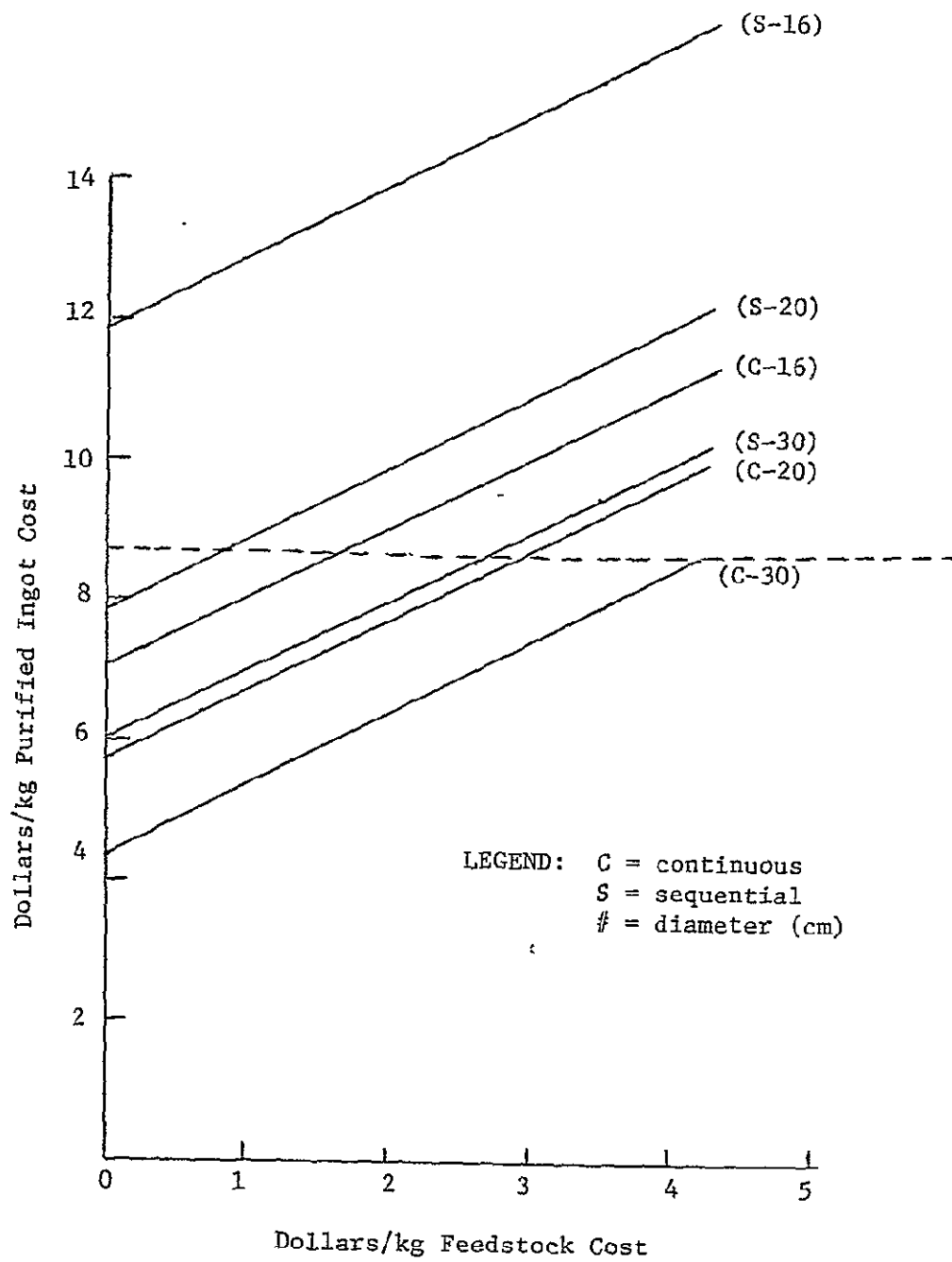


Figure 6. Cost of Purified Silicon as a Function of Net Feedstock Cost for Growth Processes Considered.

goal for purified silicon using arc-furnace feedstock material ranging in cost from \$1.50/kg to \$4.25/kg.

The softness of the data at this point makes it irrelevant as to whether 1975, 1976, or 1977 dollars are used.

2. Bridgman-Type Technique

a. Experimental

Two ingots were grown during this quarter. The ingots were 9 cm in diameter and 13 cm high. Both the ingots were crack-free although chipped at the edges. Upgraded arc-furnace silicon was used as the feed stock. For the ingot grown at a rate of 5 cm/h (720 g/h), the major impurities Fe and Al started to appear at the 36-% point. In case of the ingot grown at 2.5 cm/h (320 g/h), impurities started to appear at the 49-% point. The low yield of purified silicon is considered to be due to impurity trapping at the grain boundaries of the polycrystalline ingot and to excessive impurity build-up at the solid-liquid interface.

b. Cost Analysis

Purification of upgraded arc-furnace silicon by unidirection freezing is considered to be the part of the overall process to produce solar-grade silicon. In Bridgman-type growth, silicon contained in a crucible is lowered out of the heater zone at a controlled rate and is thereby unidirectionally solidified. Effective silicon purification can be obtained due to the low segregation coefficients of most of the impurities. However, the degree of purification is a function of growth rate, ingot diameter, impurity concentration in the melt, and crystallite size of the solidified ingot. Further work is required to define the optimum growth conditions.

Cost analyses are carried out at two different growth rates at ingot diameters of 25, 30 and 50 cm. The corresponding crucible capacities considered are 45, 81, and 450 kg of silicon. The cost numbers were calculated based on the following assumptions:

- Modified arc-furnace silicon can be effectively purified by the Bridgman-type process to yield 90-% usable silicon.
- Installed capital cost for the process was estimated at 2.5 times the equipment cost and depreciated over a period of seven years.

- Furnace cool-down, clean-up and maintenance was considered to be 20% of the total growth cycle.
- Power consumption was estimated at 25 kWh/kg Si for a 45-kg charge and 20 kWh/kg for a 450-kg charge. The power cost was estimated at \$0.025/kWh.

The cost data are reported in Tables 17-21 similar to that done for the Czochralski-type process. The results are plotted in Fig. 7. The weight of the silicon charge and rate of the ingot growth are the two single most important factors which affect the cost of the purified silicon. The power consumption is also a significant cost item. At a growth rate of 5 cm/h using a silicon charge weighing 45 kg, the purification cost was calculated to be \$3.96/kg silicon. At higher growth rate of 11.5 cm/h from a 450-kg crucible charge, silicon can be purified at a cost as low as \$1.48/kg Si. Fig. 8 shows the effect of feed stock price on purified silicon cost. For a total purified silicon cost of \$5/kg using a 450-kg charge and a growth rate of 11 cm/h, the cost of starting arc-furnace silicon can be as high as \$3.50/kg.

Table 17. Equipment Process Parameters for Bridgman Process

Equipment Process Parameters	Growth Rate = 5 cm/h			Growth Rate = 11.5 cm/h		
Ingot diameter (cm)	25	30	50	25	30	50
height (cm)	40	50	100	40	50	100
Charge Weight (kg)	45	81	450	45	81	450
Total Cycle Time - Melt Down Growth, Loading/Unloading (h)	11	13.6	25.2	6.46	7.85	13.7
Make Rate (kg/h)	4.09	5.95	17.85	6.96	10.31	32.84
Cool-Down, Clean-Up and Maintenance (h) (20% Total Cycle Time)	2.2	2.72	5.04	1.29	1.57	2.74
Effective Make Rate (kg/h)	3.68	4.96	14.88	5.80	8.59	27.37
Silicon Production (kg/y)	32,236	43,449	130,348	50,808	75,248	239,761

Table 18. Labor Costs for the Bridgman Process

Labor Related Cost Parameters	Growth Rate = 5 cm/h			Growth Rate = 11.5 cm/h		
	25 40	30 50	50 100	25 40	30 50	50 100
Ingot Diameter (cm)						
Ingot Height (cm)						
Operators/Machine	0.25	0.25	0.25	0.25	0.25	0.25
Operator Hours/Machine/y (h)	2190	2190	2190	2190	2190	2190
Direct Labor Cost/Machine/y (\$) (\$6.90/h Labor Rate)	15,111	15,111	15,111	15,111	15,111	15,111
Supervisor/Maintenance Costs (\$) 0.5 x Direct Labor Cost	7,555	7,555	7,555	7,555	7,555	7,555
Total Direct Cost (\$)	22,666	22,666	22,666	22,666	22,666	22,666
Overhead Cost (\$) (100% Total Direct Cost)	22,666	22,666	22,666	22,666	22,666	22,666
Total Labor Cost (\$)	45,333	45,333	45,333	45,333	45,333	45,333
Labor Cost/kg Si Produced (\$)	1.40	1.04	0.34	0.89	0.60	0.19

Table 19. Capital Costs for the Bridgman Process

Capital Cost	Growth Rate = 5 cm/h			Growth Rate = 11.5 cm/h		
Ingot Diameter (cm)	25	30	50	25	30	50
Ingot Height (cm)	40	50	100	40	50	100
Equipment Cost (\$1000)	50	75	100	50	75	100
Installed Cost (\$1000) 2.5 x Equipment Cost	125	187.5	250	125	197.5	250
Capital Cost/kg Si (\$) 7-yr. Straight-line Depreciation	0.55	0.61	0.27	0.35	0.35	0.14

Table 20. Expendable Items & Maintenance Costs for Bridgman Process

Cost Item	Growth Rate = 5 cm/h			Growth Rate = 11.5 cm/h		
Ingot Diameter (cm)	25	30	50	25	30	50
Ingot Height (cm)	40	50	100	40	50	100
Crucible Cost (\$) (1 per cycle)	30	50	200	30	50	200
Heater Assembly (\$) (1 per 100 cycles)	800	1200	2000	800	1200	2000
Misc./Cycle (\$) (Water, Argon, etc.)	10	17	25	8	15	20
Total Expendable Cost (\$) (per cycle)	48	79	245	46	77	240
Silicon Produced 1 Cycle (kg)	45	81	450	45	81	450
Cost (\$/kg)	1.18	1.08	0.60	1.13	1.05	0.59
Maintenance Costs (\$) (0.14 x Capital Equipment Cost)	7,000	10,500	14,000	7,000	10,500	14,000
Maintenance Costs (\$/kg)	0.21	0.24	0.10	0.13	0.14	0.06
Energy Cost at 2.5¢/kWh (\$/kg)	0.62	0.55	0.50	0.62	0.55	0.50

Table 21. Cost Summary for Bridgman Process

Cost Items	Growth Rate = 5 cm/h			Growth Rate = 11.5 cm/h		
	25	30	50	25	30	50
Ingot Diameter (cm)	40	50	100	40	50	100
Ingot Height (cm)						
Capital/kg Si (\$)	0.55	0.61	0.27	0.35	0.35	0.14
Labor/kg Si (\$)	1.40	1.04	0.34	0.89	0.60	0.19
Expendables/kg Si (\$)	1.18	1.08	0.60	1.13	1.05	0.59
Maintenance/kg Si (\$)	0.21	0.24	0.10	0.13	0.14	0.06
Energy/kg Si (\$)	0.62	0.55	0.50	0.62	0.55	0.50
Total Cost/kg Si (\$)	3.96	3.52	1.81	3.12	2.69	1.48

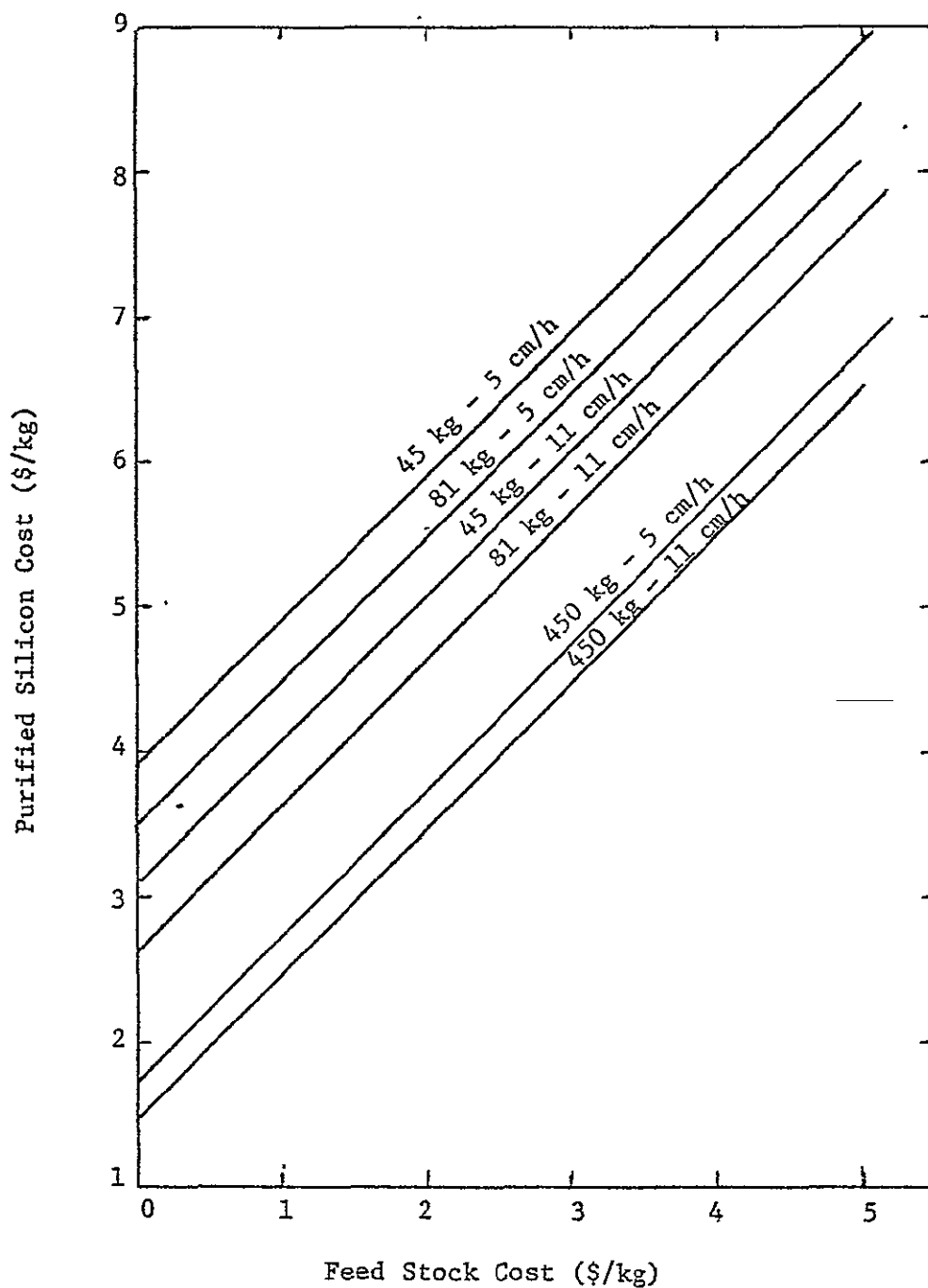


Fig. 7. Cost of Bridgman-Purified Silicon as a Function of Net Feedstock Cost

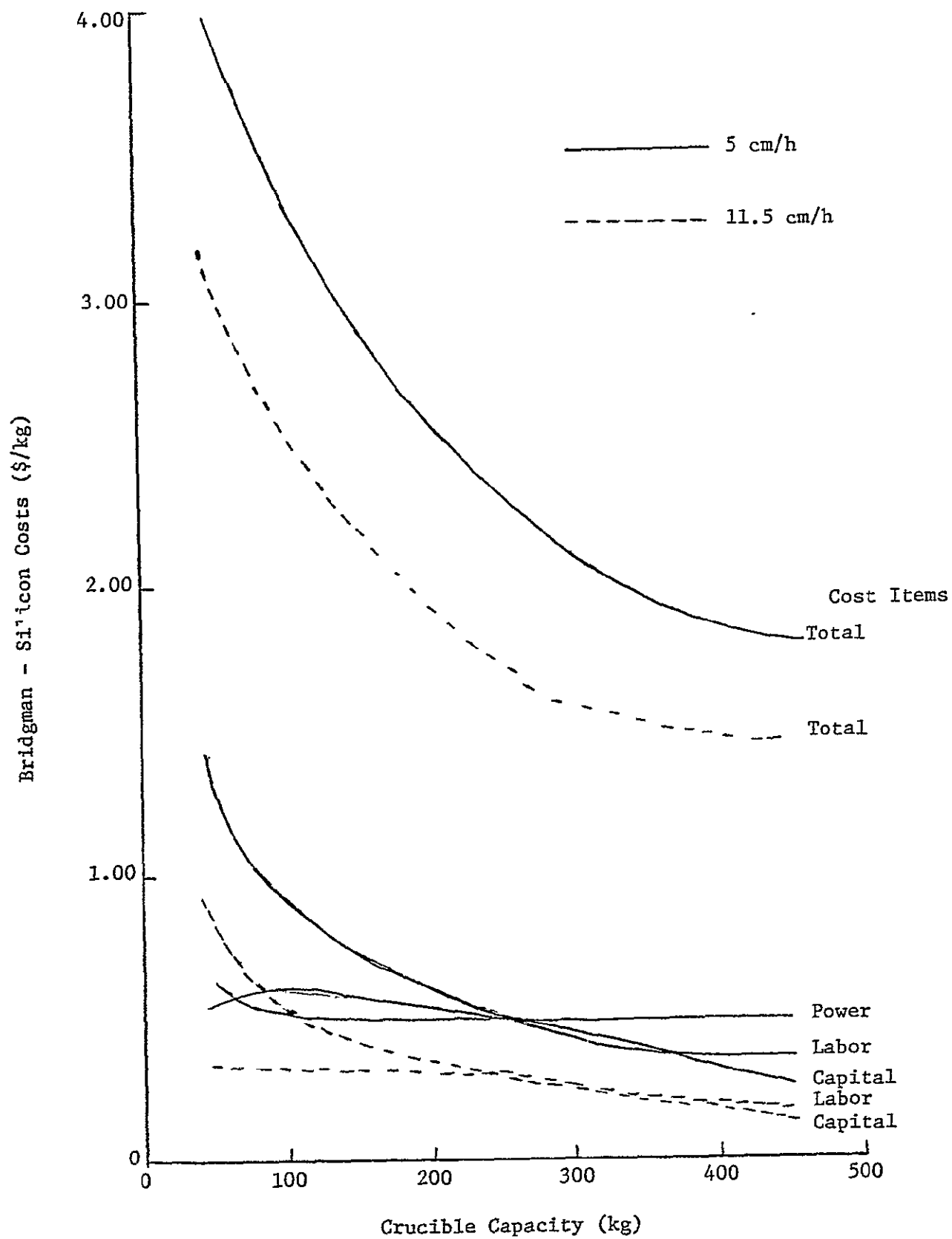


Fig. 8. Major Cost Breakdown for Bridgman-Purified Silicon as a Function of Silicon Charge at Different Growth Rates

E. Task E - Silicon Analysis

Most raw materials, arc-furnace silicon, and ingot material from the Bridgman and Czochralski-type purification methods are analyzed by emission spectroscopy. The limit of detection for the impurities generally range from 1-10 ppmw depending upon the matrix. This limitation poses a severe problem since it is in the 1-10 ppmw range, or less, that most impurities must be in order to meet the goals for this SoG-Si process.

A standard batch MG-Si was prepared (2) and sent with other samples to National Spectrographic Laboratories, Inc. for analysis via emission spectroscopy. Phosphorus, actually, is analyzed by a wet chemical technique. Statistical data were reported previously for 12 analyses of the standard MG-Si (2). Table 22 expands this number to nineteen.

Table 22. Emission Spectrographic Analysis of 19 Samples of a MG-Si Standard

Imp- urity	Mean \pm 1 σ (ppmw)	$\sigma \times 100$ Mean	Min.	Max.	$\frac{\text{Max.}}{\text{Min.}}$
Al	3400 \pm 1200	34	1700	6300	4
B	35 \pm 28	80	9	92	10
Ca	480 \pm 250	52	210	1200	6
Cr	290 \pm 90	32	90	420	5
Cu	65 \pm 37	57	20	150	8
Fe	7100 \pm 1400	20	5000	9600	2
Mg	150 \pm 80	56	40	390	10
Mn	180 \pm 40	20	110	220	2
Ni	76 \pm 28	37	40	140	4
P	38 \pm 14	38	10	60	6
Ti	330 \pm 130	39	40	550	14
V	170 \pm 80	46	80	330	4
Zr	20	-	<10	40	>4

Analyses are presented for 13 impurities: the mean and one standard deviation, the standard deviation expressed as a percentage of the mean, the minimum and maximum concentrations, and finally the ratio of the maximum and minimum values. Since the goal of this contract is to lower boron in silicon from 22 to 0.7 ppmw (0.03 to 0.3 ohm-cm), the lack of measurement precision shown in the table makes it very difficult to evaluate attainment of the goal. Fortunately boron can be determined by

electrical resistivity measurements of float-zoned silicon. Determination of the concentration levels of other impurities cannot be conveniently done, however.

The faith one can put in day-to-day analyses was recently pointed out by the phosphorus levels found in two additional samples of the standard MG-Si: 2 and 140 ppmw.

Changing analysts is not the answer to the analytical problem since the currently used laboratory is one of the best in the business for silicon analyses. A better method is required which can provide precise and accurate data at a low price with a detection limit of about 0.1 ppmw for most impurities. This may be a lot to ask for.

IV. CONCLUSIONS AND RECOMMENDATIONS

Little work has taken place to supply high-purity quartz to a very low-volume market. Sources of large volume exist and can be developed as a demand develops. Current supply exceeds demand and is projected to do so indefinitely.

Experiments have indicated that charcoal and quartz can be smelted to yield a much improved quality of MG-Si. Further experiments are necessary to determine specific operating conditions to optimize this process. Additional purification tests are required to maximize charcoal purification while minimizing structural change. Alternate carbon reductants should be identified.

The economics of unidirectional solidification look promising. Further work should take place with suppliers of crystal-growth equipment to more accurately determine the potential and costs related to scaling-up such equipment.

The overall contract is successfully proceeding toward its overall goal. It is recommended that it continue according to Program Plan.

V. REFERENCES

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VI. PROGRAM SCHEDULE

Man-hour and dollar expenditures for this and the previous quarter are shown below.

	<u>Man-Hours</u>	<u>Dollars</u>
Past	3642	167532
Current	1125	63452
Total	4767	230984

The month-by-month data are shown in Fig. 9.

The updated Program Plan is illustrated in Fig. 10. Although minor time differences exist between actual and predicted milestones after eleven months of effort, the Program is still considered to be proceeding very close to schedule with no unforeseen obstacles. Arc-furnace experiments have been delayed but have been fairly successful to date. No selection will be made between solidification methods in the near future.

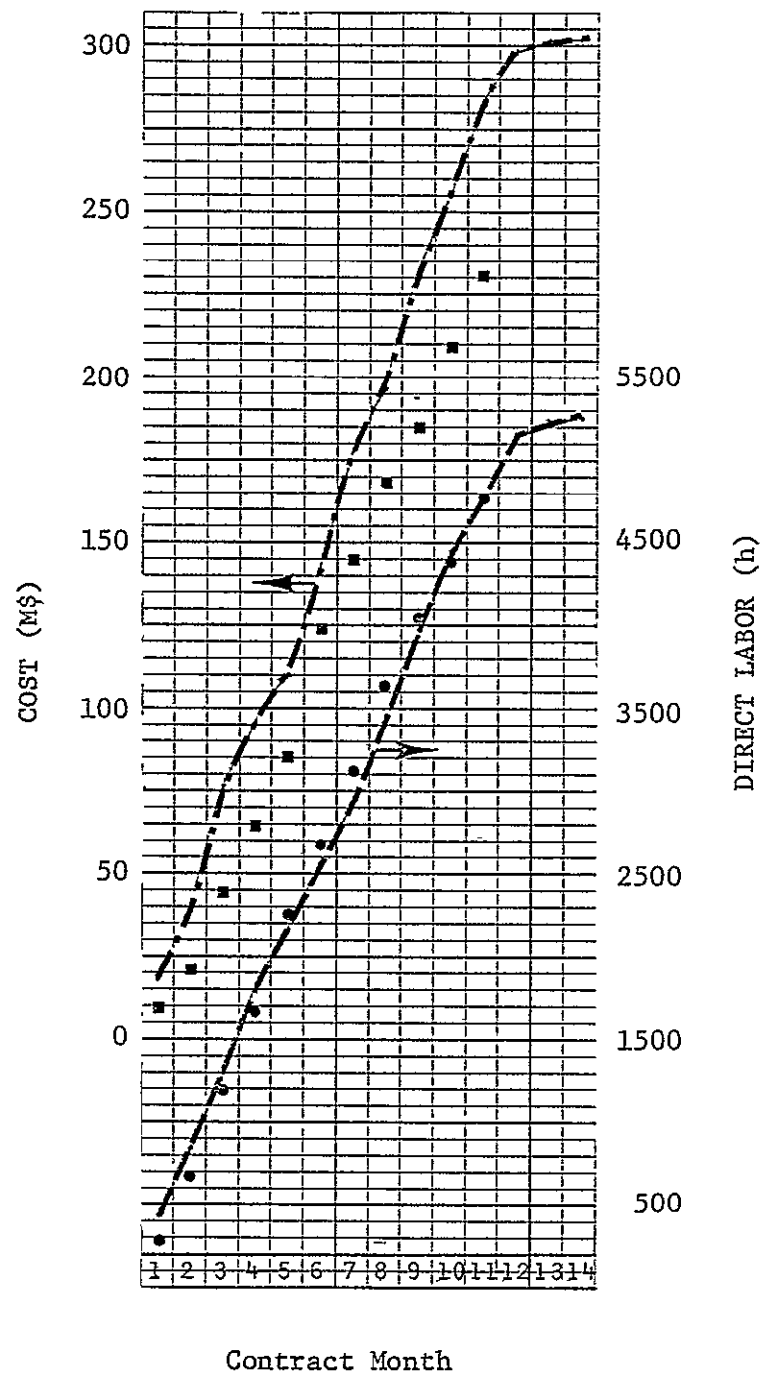


Fig. 9. Cumulative Cost and Labor

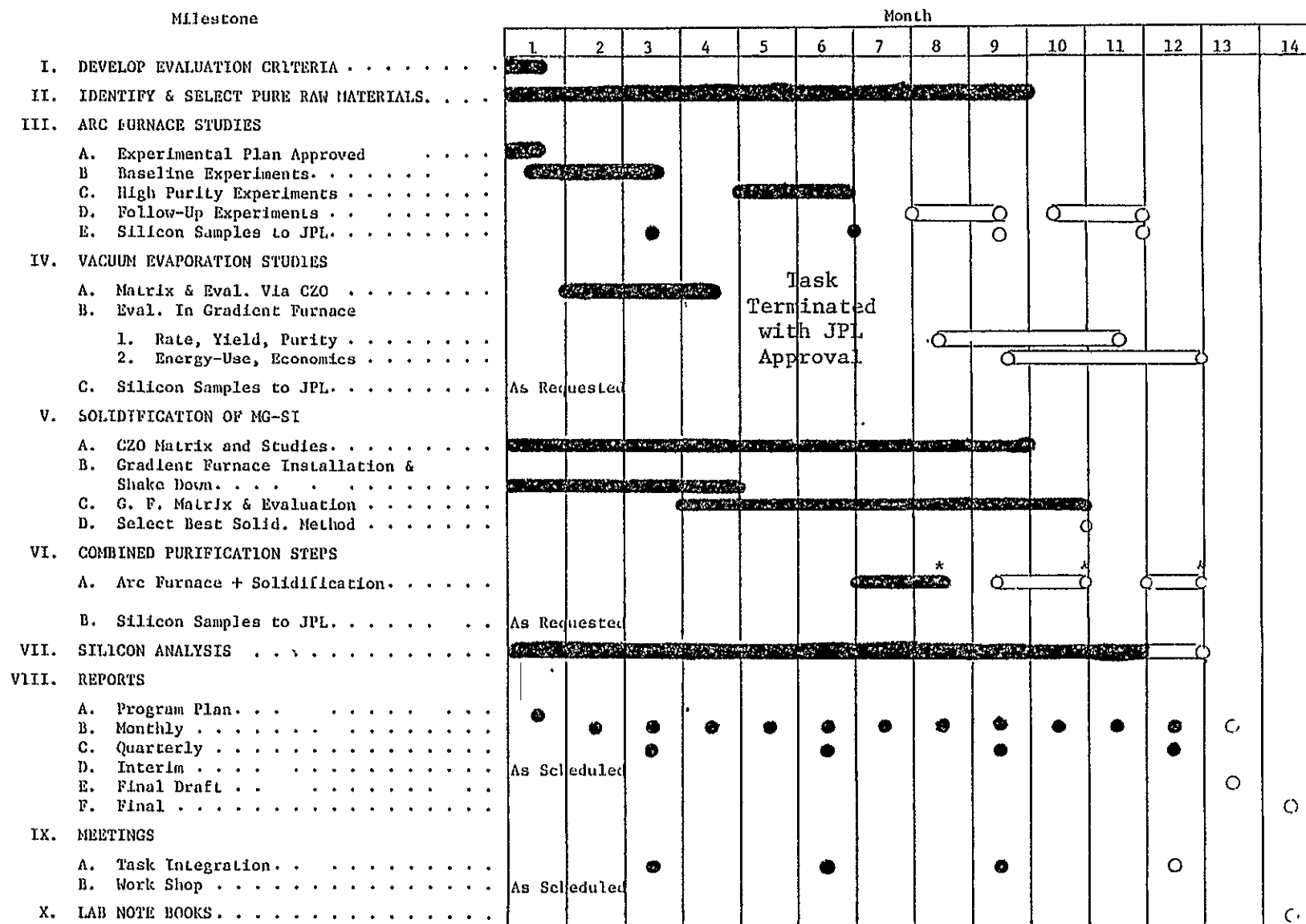


Figure 10, Technical Program Milestone Chart

VII. PLANS

The following efforts are planned in the various task areas during the next quarter.

A. Task A - Raw Materials Identification and Selection

1. High-purity quartz samples will be tested to determine their decrepitation properties.
2. Charcoal samples purified by various methods will be chemically analyzed and further characterized by smelting.
3. Other carbon sources will be investigated.

B. Task B - Arc Furnace Studies

1. Further experiments will be performed to learn more about smelting conditions using charcoal as a reducer.
2. Attempts will be made to produce high-purity silicon in the arc furnace.

C. Task C - Vacuum Evaporation Studies

Work on this task was terminated.

D. Task D - Unidirectional Solidification Studies

1. Czochralski-Type Technique

- a. High-quality material from Task B will be purified.
- b. Discussions will take place with vendors to determine the probability of scaling to higher-capacity equipment.

2. Bridgman-Type Technique

Graphite heating elements will be replaced. These were severely oxidized due to an air leak this quarter.

E. Task E - Silicon Analysis

This task will continue in support of the others.

VIII. NEW TECHNOLOGY

No reportable items of new technology have been identified.

IX. ACKNOWLEDGEMENT

Appreciation is extended to L. Crossman, A. Rauchholz, and J. Henige of Dow Corning for their able assistance. Significant contributions have also been made by N. Keyser, A. Winkler, F. Charmichael, W. Meridith, and J. Cline of Interlake, Inc. and by A. Schei and K. Larsen of Elkem-Spigerverket A/S.

X. APPENDICES

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A. Tables of Foreign and Domestic Contacts for High-Purity Silica

Table A1. Contacts for Foreign Sources of High-Purity Quartz and Quartzite

<u>Location and Company</u>	<u>Impurity (ppm)</u>				<u>Comments</u>
	<u>Al</u>	<u>B</u>	<u>Fe</u>	<u>P</u>	
ANGOLA					
*Thermal American Fused Quartz Montville, NJ 07045	8	0.5	1	0.005	\$1.50/kg (too expensive but extremely pure)
AUSTRALIA					
General Superintendence Co. Sydney	120	<1	<10	<2	Future contact
BRAZIL					
*Empresa Brasileira De Mineracao, SA 20,000 Rio De Janeiro RJ	-	-	-	-	U.S. Representative, Pulsar Trading
*Murray American Corp. Chatham, NJ 07928	-	-	-	-	Supplies clear quartz at \$8.25/kg; too expensive
*Pan American Trade Development New York, NY 10000	-	-	-	-	Supplies clear quartz from \$4.85-29/kg and milky quartz at \$1.01 kg; too expensive
*Pulsar Trading Brooklyn, NY 11200	-	-	-	-	Milky quartz \$1.17 kg; too expensive
*Strickland Enterprises New York, NY 10007	-	-	-	-	Clear quartz: \$1.17 kg` Semiclear quartz: 92¢/kg; both too expensive
CANADA					
Baskatong Quartz Products, Ltd. Montreal, Que.	-	-	-	-	Future contact
Comet Quartz, Ltd. Whitby, Ontario L1N5S	30	<1	<5	5	Clear quartz at 75¢/kg
	-	<1	19	5	Semiclear quartz at 62¢/kg
	-	1	12	9	Milky quartz at 55¢/kg
	-	2	5	2	Milky quartz at 20¢/kg
Gex Silicium, Ltd. Dorval, P.Q.	-	-	-	-	Future contact

* Eliminated from further consideration.

Table A1. (Cont.)

<u>Location and Company</u>	<u>Impurity (ppm)</u>				<u>Comments</u>
	<u>Al</u>	<u>B</u>	<u>Fe</u>	<u>P</u>	
Independent Design and Review Mount Laurel, NJ 08054	30 180	7 10	15 80	5 <10	Source near Quebec City at 10^6 Mt Second sample
*Indusmin, Ltd. Toronto, Ont. M4W1H2	3000	-	140	40	\$7.70/Mt of 98% SiO_2 ; 300 ppm Ti; sand only
Ireco Chemicals of Canada Point Claire, Que. H9R4S2	-	-	-	-	Future contact
Ministry of Industry and Commerce Montreal, Que. H3B3M6	-	-	-	-	Future contact
SKW	-	-	-	-	Future contact
Silnor, Inc. Chicoutimi, P.Q.	-	-	-	-	Future contact
Mount Rose Mining Co., Ltd. North Vancouver, BC V7J2J6	30	<1	3	5	80,000 Mt proven reserve at 66¢/kg
FRANCE					
N. C. Trading Co., Inc. New York, NY 10022	-	-	-	-	Information requested
MEXICO					
Direccion De Promocion Minera Puebla, Pue.	-	-	-	-	Future contact
Minera Thalmex SACV	-	-	-	-	Future contact
RHODESIA					
Silicon and Base Metals Co. Salisbury	230	-	8	-	7×10^6 Mt reserve
SOUTH AFRICA					
N. C. Trading Co., Inc. New York, NY 10022	130 40	1 4	18 40	2 <5	Costs 22¢/kg delivered Second Sample

Table A1. (Cont.)

<u>Location and Company</u>	<u>Impurity (ppm)</u>				<u>Comments</u>
	<u>Al</u>	<u>B</u>	<u>Fe</u>	<u>P</u>	
R. W. Greeff and Co., Inc. Dolton, IL 60419	-	-	5-10	-	Future contact
*UNITED NATIONS New York, NY 10017	-	-	-	-	No study made on quartz and silica deposits

Table A2. Contacts for Domestic Sources of High-Purity Quartz and Quartzite.

Location and Company	Impurity (ppm)				Comments
	Al	B	Fe	P	
UNITED STATES					
ALABAMA					
R&S Materials, Inc.	400	2	700	23	Quartzite gravel supplied to MG-Si plants Brown Pebble White Pebble
Montgomery 36109	-	<1	1250	20	
	-	<1	45	42	
ARIZONA					
Don Kelland Materials Tacna 85352	-	-	-	-	Future contact
Hemphill Bros., Inc. Kingman 86402	-	2	8	3	Milky quartz
ARKANSAS					
Arkansas Geological Comm.	-	4	10	9	Vein of milky quartz: 1000 tons Vein of milky quartz: 8000 tons Vein of milky quartz: 1500 tons Vein of milky quartz: 750 tons Vein of milky quartz: 2000 tons Vein of milky quartz: 10000 tons Quartz veins in an area 60 miles wide and 80 miles long
Little Rock 72204	-	2	10	7	
	-	2	12	6	
	-	4	8	3	
	-	2	9	<3	
	-	3	12	4	
Coleman Crystal Yard Jessieville 71949	-	1	-	2	
*Malvern Gravel Company	1000	-	2900	-	Sell only gravel at \$4.95/Mt; too impure 9 x 10 ⁶ Mt
Malvern 72104	-	3	21	29	
Malvern Minerals Co.	10	<1	10	<10	Clear quartz 750-lb sample semiclear quartz, 15-24¢/kg 750-lb sample milky quartz, Garland Co. 15-24¢/kg 750-lb sample milky quartz, Saline Co., 15-24¢/kg Milky quartz
Hot Springs 71901	110	<1	50	<10	
	30	2	30	<10	
	20	<1	20	<5	
	-	4	<5	<3	
Ocus Stanley	-	4	5	3	Bull quartz 10,000 tons reserves Bull quartz 44¢/kg
Mount Ida 71957	-	3	9	4	

*Eliminated from further consideration.

Table A2. (cont.)

<u>Location and Company</u>	<u>Impurity (ppm)</u>				<u>Comments</u>
	<u>Al</u>	<u>B</u>	<u>Fe</u>	<u>P</u>	
ARKANSAS					
Quartz Processing Corp.	-	<1	-	<5	Clear quartz at \$4.10/kg
Hot Springs 71901	-	<1	-	<5	Semiclear quartz
	-	2	-	<5	Milky quartz at 95¢/kg
	-	<1	15	<5	Rejected quartz at 22¢/kg
	-	<1	<5	<5	Bull quartz at 11¢/kg
					Produce 500 tons/y
*Silica Products	-	-	-	-	Sell only silica sand
Guion 72540					
CALIFORNIA					
Calif. Div. of Mines and Geology	-	-	-	-	Information supplied
Sacramento 95814					
Hemphill Brothers, Inc.	-	-	-	18	Mined Calif. source sold to MG-Si producer
Seattle, WA 98134					
*Monolith Portland Cement Co.	-	-	3%	-	Only 90% SiO ₂ ; too impure
Glendale 91202					
*Vinnell Mining & Minerals	-	-	5000	-	5 x 10 ⁷ Mt with high Fe; too impure
Alhambra 91802					
COLORADO					
Columine Glass Co.	120	3	350	15	Discolored surface but white inside;
Wheat Ridge 80033					99.3% SiO ₂
IDAHO					
*DeMonte Properties	-	-	-	-	Only sand available
Emmett 83617					
*Glory Mining	-	-	280	-	Quartz Mountain is not easily accessible
Lovell 82431					
Hemphill Brothers, Inc.	-	-	-	-	Deposit of 99.5% SiO ₂ to be opened next
Seattle, WA 98134					year at McCall

*Eliminated from further consideration.

Table A2. (cont.)

<u>Location and Company</u>	<u>Impurity (ppm)</u>				<u>Comments</u>
	<u>Al</u>	<u>B</u>	<u>Fe</u>	<u>P</u>	
*Idaho Bur. of Mines & Geology Moscow 83843	-	-	-	-	Sources said to be too impure and too inaccessible
McKelsey, John F. MacKay 83251	-	2	-	23	Millions of tons claimed to be available
*Nopah Range	-	-	-	-	Sample from field not pure
*Resting Spring Range	-	-	-	-	Sample from field not pure
ILLINOIS					
*Ottawa Silica Co. Ottawa 61350	120	-	70	-	99.9% SiO ₂ sand; 110 ppm Ti too high
IOWA					
*Iowa Geological Survey Iowa City 52242	-	-	-	-	State has only friable sand, no lump quartzite
KANSAS					
*State Geological Survey Lawrence 66044	-	-	-	-	State has no lump or high-grade material; sand has high Fe
*ThermoDynamics Corp. Shaunee Mission 66200	-	-	-	-	Buy quartz from Arkansas and Brazil
KENTUCKY					
*Pikeville Concrete Co. Elk Horn 42733	120	1-4	20	20	Limited supply of quartzite at \$2-3/Mt; 90 ppm Ti
MASSACHUSETTS					
*Sobin Chemical Boston	10 170	<1 <1	30 50	<5 <5	Process sand to "Ultra Pure Sand"; \$1.50/kg Process sand to "Quintus Quartz Sand"; 22¢/kg
MISSOURI					
*Div. of Geology and Land Survey Rolla 65401	-	-	-	-	State only has sandstone, no silica pebbles or gravel

*Eliminated from further consideration.

Table A2. (cont.)

<u>Location and Company</u>	<u>Impurity (ppm)</u>				<u>Comments</u>
	<u>Al</u>	<u>B</u>	<u>Fe</u>	<u>P</u>	
MONTANA					
*Manufacturers Minerals Co. Renton, WA 98055	-	-	600	-	New mine opening; material has high Fe
Burlington Northern, Inc. Billings 59101	-	-	-	-	Information received
Holand, Donald Fargo, ND 58102	-	1	66	<5	New quartzite source being developed in Montana
NEBRASKA					
*U. of N., Conservation & Survey Div. Lincoln 68508	-	-	-	-	State has no good deposits of silica or quartzite
NEVADA					
*Arrow Canyon	-	3	97	14	Sample from field not pure
*Bare Mountain	-	-	-	-	Sample from field not pure
*Hawthorne Silica Co. Hawthorne 89415	-	-	-	-	Mine of high-quality quartzite; accessible only during summer
*Pahranagat Range	-	-	-	-	Sample from field not pure
*Simplot Silica Products, Inc. Overton 89040	-	-	-	-	A sandstone processor; 97-99% SiO ₂
Sunnyside deposits and quarries	140	<1	140	9	U.S. Geological Survey estimates 12 x 10 ⁶ cubic miles of quartzite over five-state area (1 x 10 ¹⁷ Mt)
NEW HAMPSHIRE					
Bond Optics Lebanon 03766	90	4	20	-	2 x 10 ⁶ Mt of quartz at 48¢/kg
	-	2	5	3	Second sample

*Eliminated from further consideration.

Table A2. (Cont.)

<u>Location and Company</u>	<u>Impurity (ppm)</u>				<u>Comments</u>
	<u>Al</u>	<u>B</u>	<u>Fe</u>	<u>P</u>	
NEW JERSEY					
*Amersil Quartz Hillside 07205	-	-	-	-	Purchase quartz from abroad
*Quartz Products Corp. Plainfield 07000	-	-	-	-	Purchase Quartz from Arkansas
*U.S. Fused Quartz Co. Pempton Plains 07444	-	-	-	-	Purchase Quartz from Arkansas
*Thermal American Montville 07045	-	-	-	-	Purchase sand only
*Whittaker, Clark and Daniels South Plainfield 07080	-	-	-	-	Sell only sand
NEW YORK					
Ray Vogile & Sons, Inc. Cowanda 14070	-	-	-	-	Information requested
NEW MEXICO					
Mica, Inc. Santa Fe 87501	-	-	-	-	Milky quartzite in the area, not being mined
*N. M. Bureau of Mines Socorro 87801	-	-	-	-	No quartzite of sufficient purity available in state
NORTH CAROLINA					
Material Sales Co. Lilesville 28091	300	3-6	400	5-190	Sell quartzite to MG-Si manufacturers; reserve of 2-3 x 10 ⁶ Mt
	-	<1	245	<5	
	-	<1	76	<5	
W.R. Bonsal Co. Lilesville 28091	-	<1	55	10	Quartzite sells at \$7.15/Mt

*Eliminated from further consideration.

Table A2. (Cont.)

<u>Location and Company</u>	<u>Impurity (ppm)</u>				<u>Comments</u>
	<u>Al</u>	<u>B</u>	<u>Fe</u>	<u>P</u>	
NORTH DAKOTA					
*N.D. Geological Survey Grand Forks 58201	-	-	-	-	State has no good deposits of silica or quartzite except above
OHIO					
*Quartz Scientific Eastlake 44094	-	-	-	-	Buy quartz from Arkansas
R. W. Sidley, Inc. Thompson 44086	-	-	-	-	Future contact
PENNSYLVANIA					
*General Refractories Pittsburgh 15219	-	-	-	-	No raw material or production facilities
*Philadelphia Quartz Co. Valley Forge 19482	-	-	-	-	Do not sell silica
SOUTH DAKOTA					
*AGSCO Des Plains, IL 60018	-	-	-	-	Only sand available
Pacer Corp. Custer 60018	-	<1	<10	<1	\$2.16/kg; have other mat'l with 400-600 ppm Fe at 11¢/kg; total quartz production of 60,000 Mt/y
UTAH					
*Crystal Peak	-	4	110	36	From the field; not pure enough
*Utah Geological & Mineral Survey Salt Lake City 84108	-	-	-	-	State has no quartzite or silica production
WASHINGTON					
Manufacturers Minerals Renton 98055	-	-	-	-	Future contact
Pacific Silica Seattle 98130	-	-	-	-	Have 99.5% SiO ₂ mines in various states; samples on order

*Eliminated from further consideration.

Table A2. (Cont.)

<u>Location and Company</u>	<u>Impurity (ppm)</u>				<u>Comments</u>
	<u>Al</u>	<u>B</u>	<u>Fe</u>	<u>P</u>	
WISCONSIN					
*3M St. Paul, MN 55119	-	-	-	-	Purchase quartzite from AGSCO
*Baraboo Quartzite Co., Ind. Baraboo 53913	-	-	-	-	Looks like granite, not pure
Foley Bros., Inc. St. Paul, MN 55100	-	-	-	-	Future contact
*Nemke's Stone Quarry Hatley 54440	-	-	-	-	Slate-type stone
*Northern Stone & Const. Hatley 54440	-	-	-	-	Slate-like stone
*Wisconsin Geological and Natural History Survey Madison 53706	-	-	-	-	Provided list of quartzite producers
WYOMING					
*Geological Survey of Wyoming Laramie 82071	-	-	-	-	State has no quartzite of required purity

*Eliminated from further consideration.

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C. Material Balance Data

TABLE C-1. INPUT WEIGHTS

	Natural Weight, Lbs.					Total Dry
	Nov. 8	Nov. 9	Nov. 10	Nov. 11	Nov. 12	Weight, Lbs.
<u>Furnace Input</u>						
Alabama Gravel	95,813	102,612	105,228	103,113	104,717	511,483
N. C. Gravel	98,941	100,417	102,309	105,228	107,156	514,051
Imperial Coal	38,115	37,350	38,804	39,375	41,225	187,633 ⁽¹⁾
Sewell Coal	36,960	37,516	38,579	39,095	40,584	186,398 ⁽¹⁾
Pet Coke	19,800	19,920	20,587	20,930	21,293	96,488 ⁽¹⁾
Wood Chips	184,208	155,664	195,745	184,758	195,799	552,699 ⁽¹⁾
#1 Italian Electrode	1,463	2,261	2,261	1,995	2,394	10,374
#2 & 3 Union Carbide Electrode	4,658	4,658	5,891	5,206	3,425	23,838
<u>Ladle Input</u>						
Spout Sand						
Used Lbs.	1,000	1,000	750	850	1,100	4,700
Tag Plugs						
Used Lbs.	96	160	112	128	96	592
Zinc Plugs						
Used Lbs.	5.43	11.43	6.00	3.75	5.81	32.42
Fe Bars						
Used Lbs.	0	0	0	2	5	7
Silica Flour						
Used Lbs.	40	20	0	100	0	160
Fe Plug Tips						
Used Lbs.	2	0	2	1	0	5
No. Oxygen Lances Replaced	3	6	6	5	3	23
Oxygen Ft. ³ Used	4,280	4,667	3,694	3,320	3,899	19,860
<u>Mold Input</u>						
Crack Filler Lbs.	800	800	800	800	800	40,000
Fume in Mold Wash Lbs.	21.6	21.6	21.6	21.6	21.6	108
Spout Patch Lbs.	30	20	0	0	0	50

(1) Adjusted for their moisture content given in Table A-2.

TABLE C-2. DAILY MOISTURE CONTENT
OF CARBONACEOUS MATERIALS

Material	Moisture Content, % Weight				
	Nov. 8	Nov. 9	Nov. 10	Nov. 11	Nov. 12
Imperial Coal	4.5	4.0	2.0	2.5	5.5
Sewell Coal	4.0	3.5	3.5	2.5	3.0
Pet Coke	7.5	5.5	4.0	6.5	6.0
Wood Chips	38.5	38.5	39.5	40.5	41.5

TABLE C-3. DAILY CARBON CONTENT
CARBONACEOUS MATERIALS

Material	Carbon, % Wt. Material				
	Nov. 8	Nov. 9	Nov. 10	Nov. 11	Nov. 12
Imperial Coal	63.03	63.36	64.68	64.35	62.37
Sewell Coal	61.92	62.24	62.24	62.89	62.57
Pet Coke	79.24	79.33	80.16	78.07	78.49
Woodchips	6.15	6.20	6.05	5.95	5.85
Italian Electrode			99.2		
Union Carbide Electrode			97.0		

TABLE C-4. . OUTPUT WEIGHTS

<u>OUTPUT</u>						Weeks
	<u>Nov. 8</u>	<u>Nov. 9</u>	<u>Nov.10</u>	<u>Nov.11</u>	<u>Nov.12</u>	<u>Total Lbs.</u>
Metal Product-Crack Filler (Grade 10 plus Reg. Grade)	70,560	69,250	75,610	73,610	73,630	362,660
Lab Fines					990	990
Mold Leaks	90	250	20	0	0	360
Sub Total (Metal from Mold)	70,848	69,698	75,828	73,808	73,828	364,010
Skull Total Removed	1,700	1,160	1,210	560	650	5,280
Skull Actual	220	1,000	1,310	560	850	3,940
Back Up Ladle Total					6,840	6,840
Back Up Ladle-Spout Sand- Metal in Backup Ladle						2,140
Metal from Mold + Actual Skull + Metal in Back Up Ladle = Metal at Spout						370,090
Fume						143,915
Multiclone						80,590
Slag			9,100		6,000	15,100

TABLE C-5
OVERALL FURNACE MASS BALANCE FOR THE WEEK OF
NOVEMBER 8-12, 1976

<u>Furnace Input</u>	<u>Total Weight, lb.</u>	<u>Distribution, %By Weight</u>
Alabama Gravel	511,483	20.74
N.C. Gravel	514,051	20.85
Imperial Coal	194,869	7.90
Sewell Coal	192,734	7.82
Pet Coke	102,530	4.16
Wood Chips	916,174	37.14
Electrodes	<u>34,212</u>	<u>1.39</u>
TOTAL	2,466,053	100.0
 <u>Furnace Output</u>		
Silicon Metal at Spout	370,090	15.01
Fume	143,915	5.84
Multiclone	80,590	3.27
Gas (Volatiles, Moisture & CO)	<u>1,880,777</u>	76.26
Sub-Total	2,475,372	
Over Accounted	<u>- 9,319</u>	<u>-0.38</u>
TOTAL	2,466,053	100.00

TABLE C-6. MATERIAL BALANCE FOR BEVERLY NO. 7 FURNACE
FOR THE WEEK OF NOV. 0-12, 1976

Furnace Input	C	Ca	Al	Fe	B	P	Cr	Cu	Ti	V	Reh	Volatiles	Moisture
Alabama Gravel		20.46	245.51	204.59	0.51	10.23	12.20	7.67	22.50	5.11			
N.C. Gravel		20.56	262.17	154.21	0.51	6.60	11.02	6.17	26.73	5.14			
Imperial Coal	123,837	63.80	063.11	337.74	4.00	10.76	22.52	2.81	82.56	1.88	4,041	58,955	7,236
Sewell Coal	120,228	123.02	987.90	540.55	5.78	20.50	27.96	2.05	65.24	1.06	5,965	60,205	6,336
Pet Coke	81,040	8.68	21.23	48.24	0.09	8.20	19.30	0.29	7.72	52.10	402	14,958	6,042
Wood Chips	55,270	2376.61	160.20	226.61	0.77	17.69	9.95	1.66	12.71	5.53	6,467	490,962	363,475
#1 Italian Electrode	10,291	15.35	11.20	5.81	0.10	0.05	---	---	---	---	81		
#2 & 3 Union Carbide Electrode	23,123	60.07	113.47	66.27	0.50	0.95	---	---	---	---	715		
TOTAL	413,797	2698.55	2664.87	1504.12	13.14	83.06	103.83	20.65	217.46	71.62	10,553	625,080	383,089
Furnace Output-Spout⁽¹⁾													
Metal at Spout (from Averaged Analysis)		1369.33	2146.52	1250.31	11.47	11.04	44.41	15.17	177.64	81.42			
Multiclone	34,339	507.72	411.01	265.95	2.26	12.09	10.48	9.67	29.82	1.61	46,250		
Fume	5,483	402.96	244.66	136.72	3.60	28.70	5.76	21.59	7.20	1.44	138,432		
TOTAL	39,822⁽²⁾	2280.01	2802.19	1660.98	17.33	53.51	60.65	46.43	214.66	84.47	184,682	625,080	383,089
Furnace Output-Mold⁽³⁾													
Metal From Mold		121.53	1174.35	1309.71	10.58	11.58	44.06	13.57	169.04	67.96			
Skull		33.10	87.86	16.55	0.06	0.43	0.79	0.13	4.73	0.47			
Metal in Backup Ladle (Spout Analysis)		7.92	12.41	7.27	0.07	0.07	0.26	0.09	1.03	0.47			
Slag		1063.04	505.85	43.79	0.23	2.07	3.93	0.33	9.36	0.76			
Multiclone	34,339	507.72	411.01	265.95	2.26	12.09	10.48	9.67	29.82	1.61	46,250		
Fume	5,483	402.96	244.66	136.72	3.60	28.70	5.76	21.59	7.20	1.44	138,432		
TOTAL	39,822⁽²⁾	2136.27	2436.14	1779.99	16.80	56.62	65.28	45.38	221.10	72.71	184,682	625,080⁽⁴⁾	383,089⁽⁴⁾

(1) Furnace output as calculated at spout.

(2) Carbon output does not include carbon gasified.

(3) Furnace output as calculated on the basis of final products.

(4) Assumed to leave the furnace with gases.